REFINER
AND NATURAL GASOLINE MANUFACTURER
A GULF PUBLISHING COMPANY PUBLICATION

VOLUME 11, No. 11 NOVEMBER, 1932

Process Equipment Needs

MANY factors point to aggressive construction of refining facilities during the year 1933. This is especially true of the cracking department, and to a lesser degree, of the general distillation department.

With over 280 concerns operating plants in the refining industry about 155 of them have no cracking equipment—and many of these concerns know that something must soon be done about it. About 125 companies operating refineries are provided with cracking facilities—a surprising number of such units are of the 1925-26 vintage; rapidly approaching that state in which they are too hazardous, too inefficient when compared to modern practice, to be much longer considered as assets.

This field will expand in 1933. It will add around 100,000 barrels capacity. It will replace around 150,000 barrels lost through obsolescence and dismantling. It will see remodeling and rehabilitation of around 100,000 barrels capacity. Further, rehabilitation and construction in distillation of all types, recovery, stabilization, power plants and piping will be of like importance.

It must be understood that rehabilitation—the replacement of obsolete equipment—does not mean enlargement of capacity for production beyond economic requirements. It means readjusting plants to produce their present output with less waste. It may in some cases involve the scrapping of machines and processes which can not be operated efficiently on a scale of production consistent with current demands for the products.

The rapid improvement of equipment during the past three years offers opportunities for increased earning power to plants that adopt modern facilities for meeting their present operating problems. Many companies have liquid funds drawing low interest which they feel would much better be invested in more profitable equipment. Changes in equipment incidentally, can be made much more easily when plants are not running at full capacity.

The primary obstacle that has been hindering aggressive construction is neither lack of funds nor failure upon the part of executives to realize that their plant must be considerably repaired and re-equipped before normal operations, and efficient operations, are possible.

A very large number of concerns have had their rehabilitation plans and new equipment specifications on paper for months. The primary obstacle has been a general mistrust of the economic situation and a real tendency to wait until orders received require specific attention.

The refining industry will enter 1933 with its inventories low, lower possibly, than at any time in the past two decades. It will enter the new year with obsolete equipment variously estimated at from 25 to 40 per cent of total operating capacity. This year has seen much vigorous construction work but for the most part equipment has been operated somewhat past that point where under good conditions it would have been abandoned or converted to less severe service. These conditions must be remedied and a preliminary study of the factors affecting construction indicates that remedial steps will be taken aggressively, during 1933.

Modern Japanese Refinery *Layout Minimizes* Handling of Materials

P. H. WOODS
Associated Oil Company

IN order to meet competition in the Far East, the Mitsubishi interests of Japan and Associated Oil Company of California joined forces, through a jointly owned subsidiary, Mitsubishi Oil Company, to construct a modern refinery for the manufacture of a complete line of first quality petroleum products. The plant has been in operation for only a few months, but it has lived up to all expectations from an operating standpoint. Facilities have been provided for every normal plant operation from the receipt of crude oil from ocean-going tankers to the shipment of finished products in bulk or package.

The layout of facilities is such that a minimum of handling of materials is required, the straight-line idea being employed. Based on this idea, the storage tanks are located next to the wharf, then in order lie the run tanks, the refining units, and, finally, the shipping department, which is served by a spur from the railroad.

The plant site occupies about 20 acres of dredger filled land adjoining the sea-wall of Tokyo Bay near Kawasaki, about midway between Tokyo and Yokohama. The fill averages 60 feet in depth and rests on a bed of sand and clay, the surface elevation being only six feet above mean high water. In consequence of these facts great care was necessary in the design of foundations and drainage structures.

DESCRIPTION OF PROCESSING

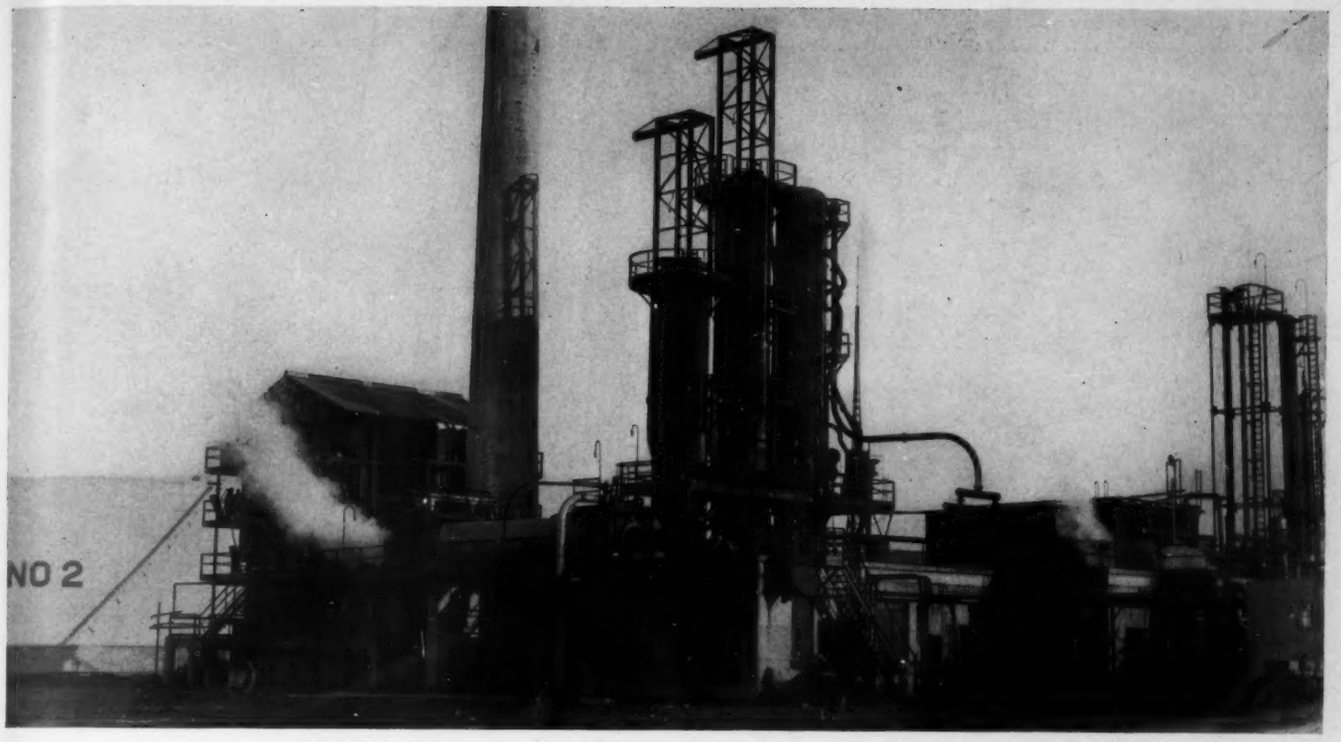
The two refining units were designed for the maximum of usefulness. The combination topping-cracking unit is charged with light crude and produces straight-run gasoline, pressure distillate, kerosene, gas oil and fuel oil. The other unit may be used either for producing lubes from heavy crude, or for re-running pressure distillate.

The topping-cracking plant is of the Cross type and has a rated capacity of 3,000 barrels per stream-day when being charged with 28° crude. The charge is pumped successively through exchangers built into the tops of the fractionating and evaporator towers, attaining temperatures of about 350° and 600° F., respectively, and then passes to a flash tower, overhead, from which it is condensed as straight-run gasoline. Side streams from this vessel are also taken off as kerosene and gas oil. Bottoms from the tower pass to a tank where they mix with re-cycle stock and are then pumped through the cracking furnace and reaction chamber to the evaporator. The furnace operates with an inlet pressure of 750 pounds and raises the temperature of the oil to approximately 850° F. Evaporator bottoms are drawn off as fuel oil, and a portion of the stream, after cooling, is returned to the vessel as reflux. The condensate from the exchanger in the top of the evaporator, which serves as a partial condenser, consists of heavy ends of the overhead vapors and is returned to the mixing tank which receives the flash tank bottoms. Uncondensed overhead vapors pass on to the fractionating tower, bottoms from which are also returned to the mixing tank. Fractionator overhead goes then to the final condenser, thence to the gas separator, where gas is taken off, and the liquid, pressure distillate, is ready to be stabilized. The latter operation is carried on in a separate absorber-stabilizer plant, the stabilized distillate being then blended after treating with straight-run gasoline as required.

The still is of conventional design, but includes all the most modern improvements as developed and constructed by the builder, a well-known American contracting firm. The heat input is 37½ million B.t.u. per hour when operating at full capacity. Tubes are of cold drawn seamless steel of five-inch O.D. and five-eighths-inch wall thickness.

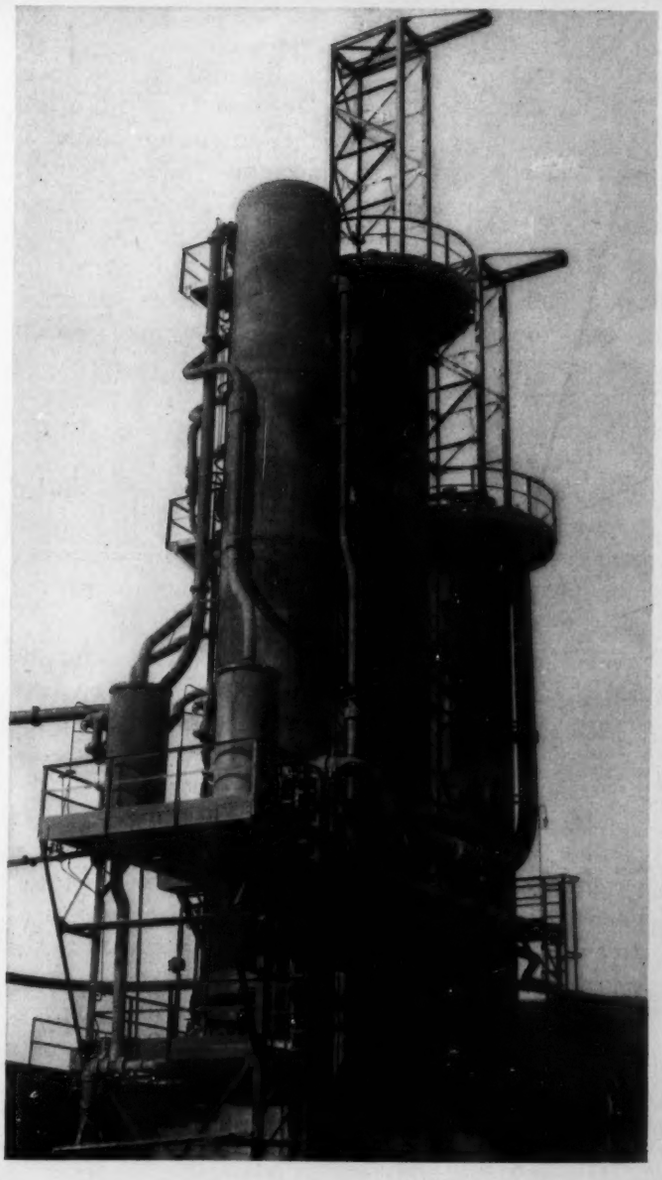
Knowing that a viscosity breaking operation might be desired at a later date on account of the advantages that a combination unit has as compared to a direct cracking unit, the designers made provision for the addition of a second heater. Should this furnace be added the reduced crude from the bottom of the flash tower would be partly cracked therein to form gas oil which would then be fully cracked in the other furnace.

The second unit, when producing lubes, combines atmospheric flash and vacuum distillation to process 1000 barrels per stream-day of 16° crude. The charge passes successively through a reflux exchanger in the top of the vacuum tower, the bottoms exchanger on the same tower, the furnace, and to the atmospheric tower. Before reaching the furnace the charge is heated in the exchangers to a temperature of 350° F., and

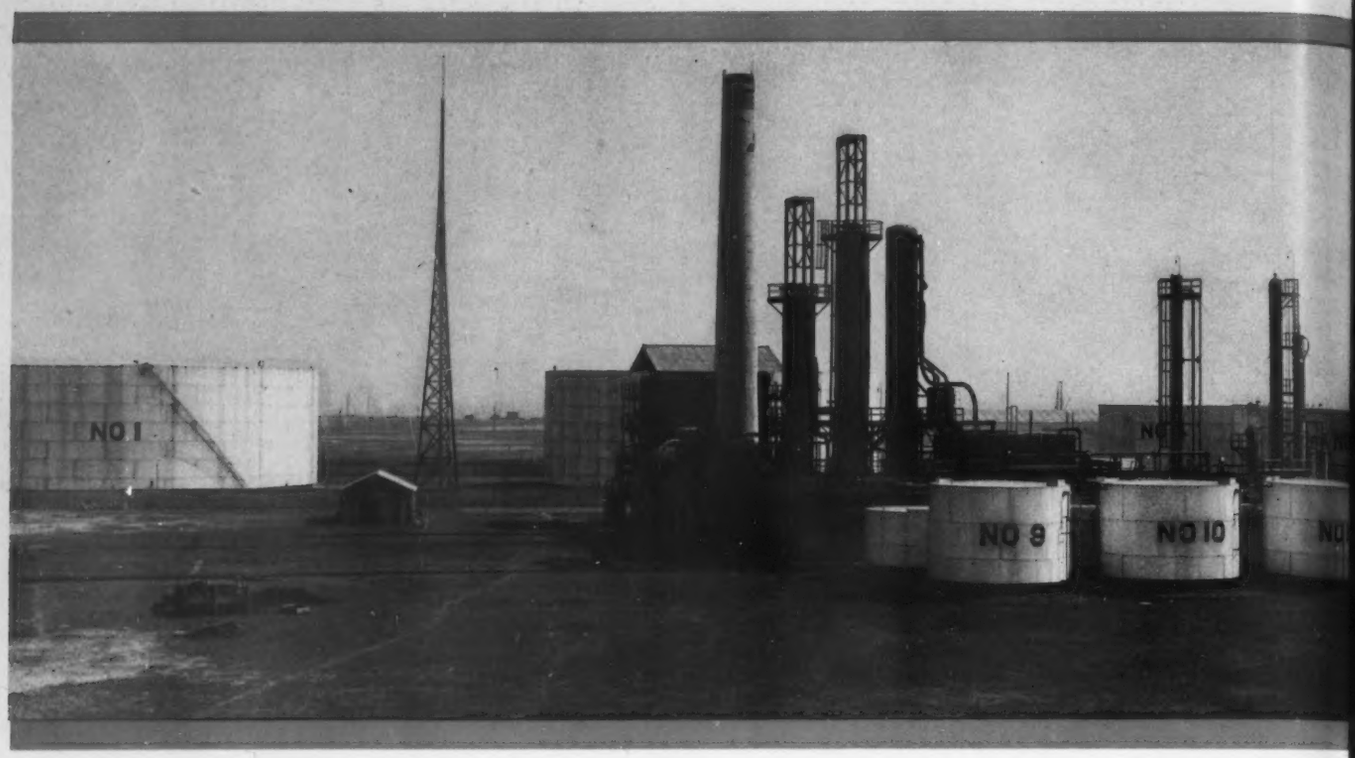


Cross Cracking Unit at Mitsubishi Oil Company, refinery, off-stream for cleaning

Associated Oil Company of California and Mitsubishi Interests of Japan, in protecting their market in the Far East, are operating an efficient complete refinery on Tokyo Bay



Evaporator and Fractionator Towers for the Combination Cracking Process.



the outlet of the furnace is run at 650° F. Bottoms from the atmospheric tower are passed through a coil in the convection section of the heater and flashed in the vacuum tower at a temperature below 700° F. Stripping steam is introduced into the base of the tower and complete fractionation occurs on the rectifying plates. The reflux exchanger in the top of the tower condenses from the overhead vapors sufficient material to serve as reflux, the uncondensed portion passing on to the final cooler where it is taken off as transformer oil. The necessary vacuum is produced by a steam ejector, booster, and barometric condenser. Side streams from the vacuum tower are taken off to be condensed as light, medium, and heavy lube stocks. Bottoms from the tower are mixed in with fuel oil from the cracking unit and used for refinery consumption. Overhead from the atmospheric tower is naphtha and a side stream is taken off as gas oil.

When re-running pressure distillate in the unit the side stream equipment is cut out of service on both towers. Capacity on this material is 2400 barrels per stream-day. The charge follows the same path as when processing lubes, flashing in the atmospheric tower. Overhead from this vessel condenses as a light cracked gasoline, ready for final treating. Atmospheric tower bottoms pass without pumping to the vacuum tower where flashing again occurs. Overhead condenses as stream is re-heated in the furnace and returned to the heavy cracked gasoline. A portion of the bottoms tower to provide the necessary heat for vaporizing.

The heat input to the furnace when operating as a lube unit is 5½ million B.t.u. per hour, and when used as a P.D. re-run unit, nine million.

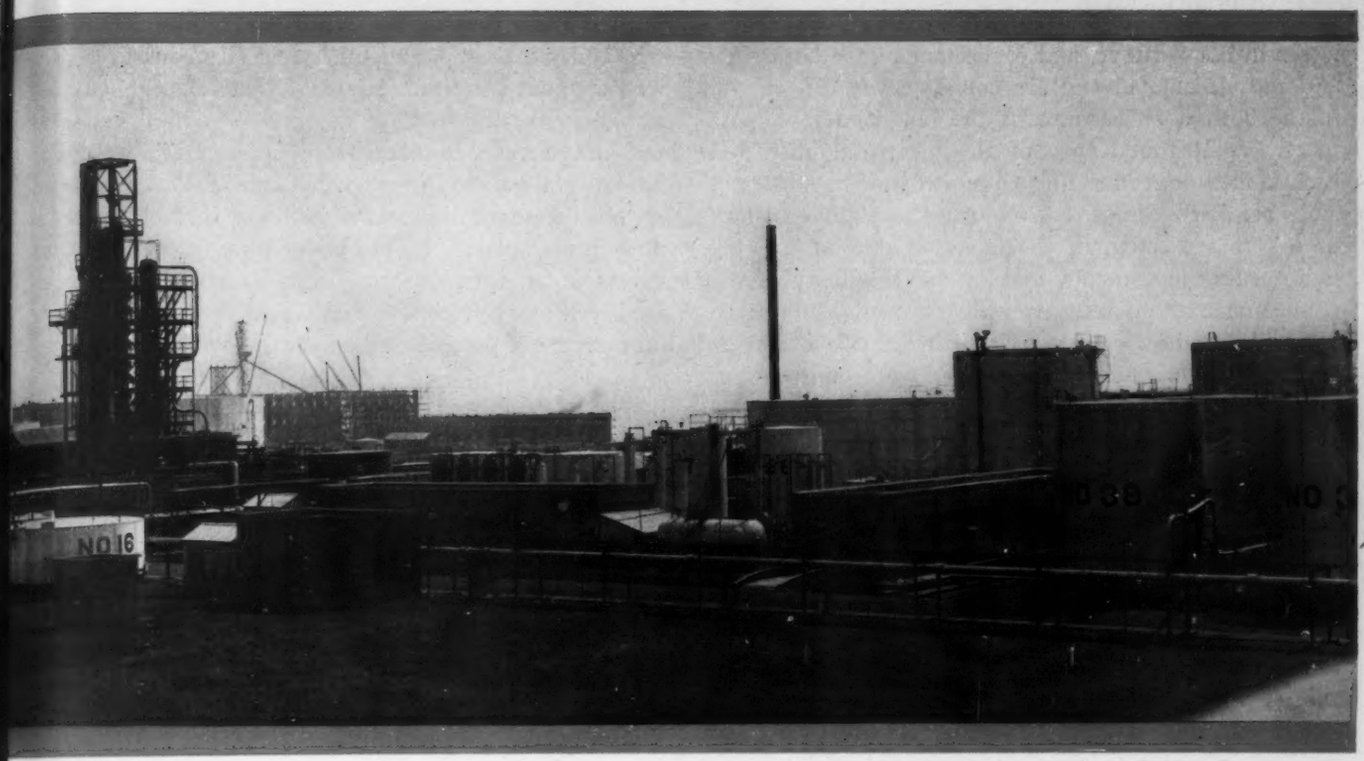
Firing equipment in both the cracking and lube-P.D. re-run furnaces will burn both oil and process gas, use of the latter effecting a considerable saving of liquid fuel which is thus released for sale. The gas is taken from the absorber where a small amount of gasoline is recovered.

The treating plant is of the continuous type, using acid as the purifying agent. Separate units process straight-run gasoline, cracked gasoline and kerosene. Treating of straight-run gasoline and kerosene is the finishing process, but for cracked gasoline the step is intermediate between stabilizing and re-running.

FOUNDATIONS AND BUILDINGS

Extensive tests were necessary to determine the load bearing capacity of the soil because of the nature of the ground and the frequency of severe earthquake shocks. These tests revealed that a bearing pressure no greater than 1750 pounds per square foot could be used. They further showed that an extensive system of lateral bracing would be required in order to prevent horizontal movement of one unit relative to another, particularly when connected by piping. Because of the depth, 60 feet, of the relatively loose soil, piling was resorted to, the piles in general being of wood and about 40 feet long. Caps are of concrete and form the foundation mat for the superstructure. Where two structures are closely connected a common mat is laid under an entire group in such a manner that even a severe earthquake shock would not displace the component parts relative to each other. Firewalls surrounding tanks are also set on piles, the cap forming the base of a retaining type of wall.

Buildings are also of unusually heavy reinforced concrete and steel design for the same reason. Corru-



Panoramic view of Mitsubishi Oil Company refinery on Toyko Bay near Kawasaki, Japan.

gated sheet asbestos is used for roofing. Utility and strength were not the only considerations in design; architecturally the structures were made to present a pleasing appearance.

The lack of adequate elevation and the heavy rainfall, amounting to around 70 inches per year, made necessary other measures than natural drainage. The condition was further complicated by the stringent governmental regulations regarding contamination of waters of the bay with oil. With the limitations thus imposed, a system was designed to handle natural run-off and process waste water with a discharge to the bay containing not over five parts per million of oil, and consisting of a system of sewers, open ditches, and an oil separation-water recovery plant. Sewers were installed in all locations where it was probable that oil would be handled, open ditches being restricted to the handling of water, particularly run-off. Where ditches discharge to sewers, fire-stopping traps are installed to eliminate any possibility of the spread of flames.

The entire system eventually discharges to a collector pit immediately ahead of a separator in which objectionable matter is removed. Sewage is pumped from the pit into the separator, the level in the latter being maintained constant by means of a float-operated valve in the centrifugal pump discharge line. The separator is in two sections, the first of which is quite large, thus permitting an extremely low velocity for a considerable period. Oil is thus given an opportunity to rise to the surface where it may be skimmed, while solids and other heavier than water material sinks to the bottom. A system of submerged baffles and wiers connects the first compartment to the second and subjects the lower strata of water containing the solids to a scrubbing action during its passage. Oil in emulsion or otherwise in suspension is released and a separation again occurs in the second compartment where it is skimmed. Settlement of solids naturally occurs, but these are periodically removed, loaded onto barges, and dumped far at sea.

The wharf is of all-concrete construction and was designed by Japanese engineers. The wharf approach is 100 feet long, connecting the 225 by 37 foot wharf to the sea-wall. The approach and wharf are of similar construction, using 18-inch square by 60-foot precast piles surmounted by a bracing system 11 feet in height and surmounted by a deck slab six inches thick. With a water depth of 30 to 38 feet, depending on the tides, sea-going vessels are enabled to tie up and discharge their cargoes of crude through short lines to the tanks.

Tanks were all built to A. P. I. specifications, and are the first in Japan to be constructed to these standards. Inside caulking, caulking strips and steeple snap rivets were also used for the first time in the Island Empire. Yet another innovation, for Japan, was introduced in the method of testing tank bottoms. Heretofore it had been customary to test by filling the entire bottom ring with water, but with these tanks only about six inches was used, since this depth affords nearly as sure a test as a five-foot head, and the greater head is a needless waste of water.

Size of tanks installed varied from the usual small general service tank to those of 80,000 barrels capacity. Light oil tanks have roofs insulated with hair-felt and

asbestos as a protection against excessive evaporation losses in hot weather, and crude tanks have both shells and roofs insulated and are equipped with steam coils in the bottom on account of the low winter temperatures. A 10-foot length of flexible metal hose joins each tank to its connecting piping to guard against possible breakage of the latter during earthquake shocks or due to settlement of the tanks. Grouping of tanks is according to contents, making for simplicity of pipe connections. Concrete firewalls surround the tanks, in pairs for the larger sizes, and by groups of several for the smaller ones. Swing pipes were omitted from all tanks.

Piping is of welded construction throughout the refinery, except where breaks are required for expansion swings, or to make lengths convenient for handling, in which cases it is screwed or flanged, respectively. All valves and fittings are flanged.

Steam reciprocating pumps are used in the refining units, centrifugals and rotaries for transferring products and general utility purposes. Certain of the pumps in the cracking unit which are subject to corrosion have valves of stainless steel. Locations of pumps are centralized in order to simplify operations and to make expansion easy. Motors driving centrifugal pumps are of the explosion-proof type to reduce the fire hazard to a minimum.

POWER AND WATER

Electric power is not generated within the refinery, inasmuch as energy is abundant and can be obtained cheaply from outside sources.

The boiler plant consists of four Garbe boilers—four drum, bent tube type—with a total normal rating of 26,000 pounds of steam per hour, and operates at 150 pounds pressure, without superheat. Exhaust steam is used for processing and for heating.

Fresh water is obtained from the company's own well, located about three miles inland, and is used for drinking, boiler make-up, and other miscellaneous uses. The well is about 200 feet deep, and yields 350 gallons per minute without affecting its level. Cooling and general usage water is taken from Toyko Bay through an intake that was so designed that it will not be affected should the sea-wall be rebuilt 50 feet further out, as is now contemplated. The pumps are protected from debris of an injurious size by a screen structure situated well away from the wall. This location will allow uninterrupted pumping when the sea-wall is rebuilt.

MISCELLANEOUS

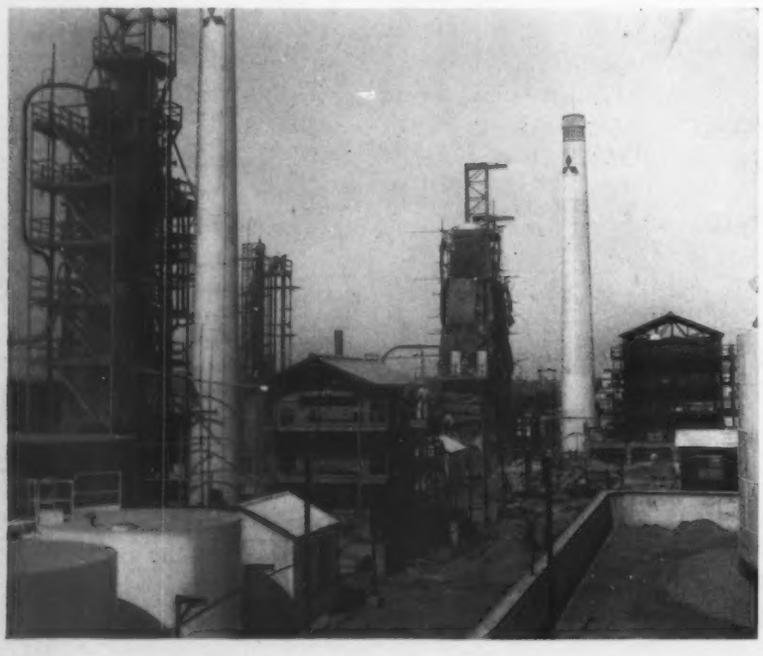
Complete package making facilities were provided where all drums, cans, and cases are made. Because of the distance from the source of supply of manufactured packages and the large stock of these articles that it would be necessary to carry, it was estimated that the investment so tied up would be better employed and funded in a few years, by purchasing the necessary machinery and making the packages on the spot at a decrease in cost over the purchased article.

To facilitate the handling of materials entering and products leaving the plant, a group of structures was located along a spur track to house filling and shipping equipment, warehouse and shops. In the latter, operating repairs and small changes to plant equipment can be made.

Construction activities were somewhat hampered during erection due to the fact that Japanese laborers refuse to work on rainy days and that there are some 150 such days in the year. In spite of this handicap, it is notable that all units were practically complete within 12 months of the breaking of ground for initial grading operations.

The first unit was started on December 14 of last year, and results obtained during the runs of the first nine months indicate the unit to be extremely flexible, and that refining efficiency can be maintained even when processing a crude of entirely different characteristics from that for which the plant was designed. Longer times on stream have also been found to be possible than was at first considered practicable. Corrosion troubles have been at a minimum, although exact data are not immediately available.

Presentation of the above data was made possible only through the kind assistance of William Wakeman, who was in charge of the design and layout of all but the contracted units, and Arthur B. Peckham, who served as field superintendent during the construction period, both of whom are on the engineering staff of Associated Oil Company.



Lubricating Oil Distillation System and Cross Cracking Plant

Cracking Still Gasses

Logical Source of Ethylene

A. L. NUGEY
Petroleum Engineer

IN this article A. L. Nugey writes of the preparation of ethylene, after experience in the design and erection of a plant built for its extraction. The author includes a discussion of the uses for ethylene, data on the thermodynamic properties of the product, and detail of installations for its extraction.

The work is presented because of the lively interest in synthesis evidenced by workers in the refining industry. While the industry may never engage in the manufacture of plastic resins, it may well study the advisability or its capability of supplying raw materials to the plastic resin industry. Ethylene, if produced in commercial quantities and cheaply, may well be a source of additional revenue, since it is the essential raw material needed in the preparation of the new plastic resin chemically termed Metastyrene. Mr. Nugey believes that the refinery is the logical source of ethylene for this and other industrial applications.

THE plastic resin industry today, even though it is in its infancy, is one of the country's most important industrial achievements. The practical development of this art is to primarily displace the use of such basic materials as wood, metals and ceramic products. Several groups of the basic resins are now extensively in use. However, none of these groups fill the requirements for a broader development of application in the plastic resin industries. The cellulose products, such as celluloid, pyroxylin, and the acetates of the first group, are too expensive and inflammable. Besides these disadvantages they usually warp after molding. The molded products from another group comprised of phenol and similar resins do not adapt themselves readily to attractive color combinations which are so important today from a merchandising standpoint. Other disadvantages are brittleness and costly molding equipment required to form them into suitable products.

No accurate statistics are available as to the amount of plastic resins sold in this country today, but quoting from figures published for the Chemical Exposition in May, 1931, the following indicates the record growth of the plastic resin industry:

Year	Business Volume In Dollars
1914	$ 14,000,000
1928	219,000,000

The government reports for 1929 show that 25,000,000 pounds of pyroxylin plastics were sold for a price range of 75 cents to $1.25 per pound, and that over 33,000,000 pounds of synthetic resins at a price range of 25 to 50 cents per pound.

The new plastic resin, chemically termed, Metastyrene, and which can only be produced commercially from condensed ethylene, and which is the new resin that will displace cellulose products, pyroxylin, and phenolic resins commands the following market price range of 80 cents to $2.00 per pound. The cost to produce Metastyrene resins will not exceed 12 cents per pound, provided the ethylene can be obtained for less than 6 cents per pound.

METASTYRENE RESIN

The chief obstacle that hindered the development of the metastyrene resin industry was the fact that ethylene, which is its raw material, was not available commercially. It is true that this resin can be made from other chemicals, but the finished resin is not as satisfactory as that which is manufactured from ethylene. The advantages of metastyrene over other resins, is that it is water proof; heat proof; and climatic proof. Besides it can be produced under lower molding pressures, it is readily blended into any color combinations, shades, opaqueness and transparency, similar to glass, but possesses greater structural strength, making it adaptable for the production of:

Toiletware	Hardware Trade
Novelties	Plumbing Fixtures
Jewelry Trade	Electrical Fittings
Optical Instruments	Stationery Supplies
Mechanical Dentistry	Printing Industry
Mechanical Appliances	Lacquer and Varnishes

The foregoing all form a part of the innumerable applications for metastyrene. The future possibilities of this resin are still to be fully developed. Time will find its use applied to furniture and many phases of building construction. Many chemical plants

have developed processes to make metastyrene using ethylene because of previous stated advantages

ETHYLENE

It is obvious new why ethylene is at present the most sought of basic materials. At present there is only one producer of ethylene, and it is shipped in metal cylinders weighing 150 pounds, and only containing 28 pounds net of ethylene. In addition to the market prices (45 to 65 cents per pound) the purchaser of ethylene must add the freight of the heavy ethylene cylinders. In order to compete with the manufacturers of other plastic resins, ethylene should be available at a very low cost. This cost must also include the freight and capital investment necessary for the carriers of the ethylene. To produce the best metastyrene resin the ethylene should have these specifications:

Ninety-eight per cent pure ethylene, two per cent ethane, absolutely free of sulphur.

Ethylene is an inflammable gas, and forms an explosive mixture with air at a concentration of approximately three per cent. Its molecular weight is 28.03 and the boiling point of minus 103.9°C (minus 155°F.) The critical temperature and pressure are 9.5°C (49.1°F.) and 744 pounds absolute respectively. Ethylene has practically the same density as air, and consequently diffuses very readily.

Besides being the basic material for the production of metastyrene resin, ethylene has many other important uses. It is extensively used for accelerating the coloring and ripening process of fruit and vegetables. One large fruit producer follows this practice. After the oranges have been picked, which incidentally have not as yet acquired the rich yellow color of complete maturity, they are placed into boxes and stored in a closed room, the temperature being maintained by an electric heater at 80°F. The heat and the moisture from the oranges cause them to sweat. Then for each 10,000 parts of air in the room, one part of ethylene gas is released to assist the coloring process.

Ethylene is also a very desirable refrigerant. It is also the starting point for making dichloride ethylene, ethylene glycol, ethyl chloride and ethylene chloride. Another important derivative is ethylene chlorhydrin which is produced by reacting ethylene and hypochlorous acid. Still another important use is that it will substitute chloroform, having the advantage under certain conditions of producing greater relaxation; and being far less toxic, thus reducing the tendency of nausea. Of course the ethylene for any anaesthetic uses must be of the anaesthetic grade, and must have a purity of 99.5 per cent plus. Up to this time no accurate data has been available upon the thermodynamic properties of ethylene, and the accompanying tables will be very useful to the petroleum industry.

There are at least five sources from which to extract ethylene, namely; natural gas; cracking suitable oils; residual gases from vapor phase cracking plants; alcohol; and by cracking of liquefied gases. The first three sources call for previous gas purification equipment, and it is not convenient to establish the metastyrene resin plant to suit market conditions. Producing ethylene from alcohol is rather expensive and the yields will be lower. So that it will leave only one source that will meet all of the imposed economical conditions.

It has been explained that the metastyrene industry will use very large quantities of ethylene, and for economic reasons it is desirable to place the ethylene plant adjacent to the resin plant, which can operate synchronously with it, and eliminate costly storage equipment.

Several hydrocarbons are suitable for production of ethylene from liquefied gases. Tests have revealed that the natural gas constituent most suitable for the raw material lies on the division line between saturated and unsaturated hydrocarbons. The following analysis indicates the constituent parts of this suitable liquefied gas as it leaves the cracking coil furnace.

ANALYSIS OF GAS LEAVING CRACKING COIL

	Per Cent By Volume
Hydrogen and Methane	8.7
Ethylene	21.5
Ethane	0.7
Propylene	7.3
Propane	1.4
Butylene	1.0
Butane	59.4

A series of analyses taken shows that the concentration of the individual unsaturated hydrocarbon constituents change during the recycling progress. In other words they can be controlled so as to obtain the maximum yield of the desired hydrocarbons. The time and temperature factors are very important indexes in producing ethylene from liquefied gases.

THE ETHYLENE EXTRACTION PLANT

In the preliminary work prior to construction of any ethylene extraction plant, the designing engineers should follow the procedure set by the architects in order to be certain that the commercial plant will meet the requirements imposed upon it. For example the cracking plant must be of intelligent design due to high heat release, the tube arrangement should be properly made, and the metals and refractories must be properly selected for the duty expected. Carbonization of tubes and the deposition of the carbon on the plates of the separating columns must be prevented. Similarly, fluctuations in the volume of the feed will affect the ratio of liquid flowing down to that of the ascending vapors in the column which greatly hinders proper selective separation. The pressure and temperature factors deter-

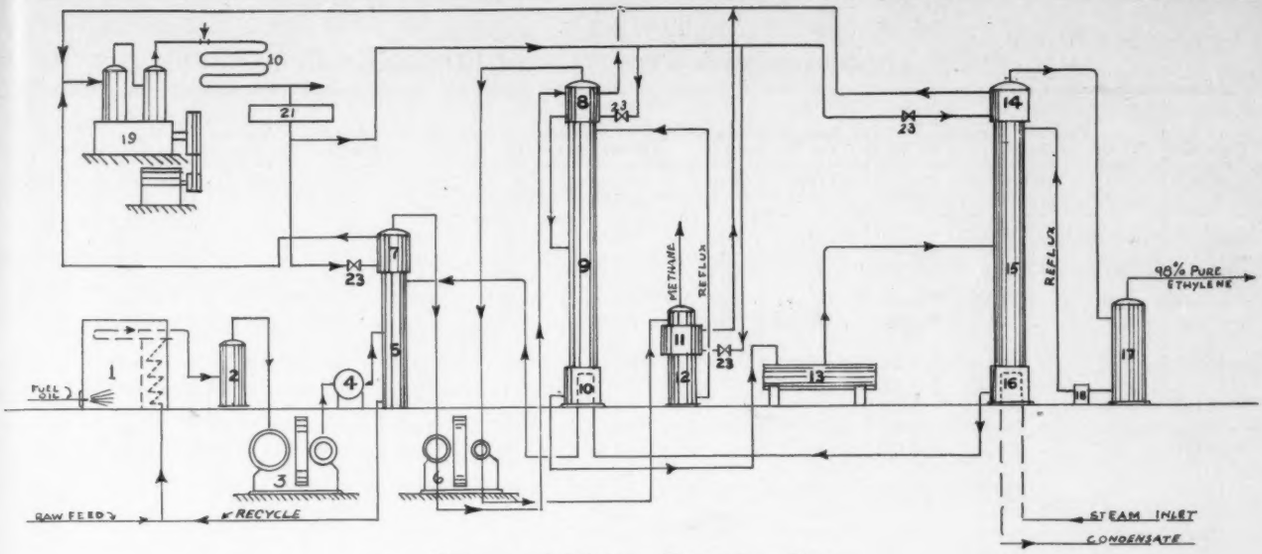


Diagram of Ethylene Extraction Plant

1—Cracking Coil Furnace
2—Accumulator
3—Gas Compressor
4—Water Cooled Condenser
5—Eliminator
6—Gas Compressor
7—Direct Expansion Cooler
8—Direct Expansion Condenser
9—Methane Column
10—Methane Column Reboiler
11—Direct Expansion Cooler
12—Reflux Separator
13—Rundown Storage Tank
14—Direct Expansion Condenser
15—Ethane Column
16—Ethane Column Reboiler
17—Reflux Separator
18—Reflux Pump
19—Propane Refrigerating Compressor
20—Water Cooled Propane Condenser
21—Propane Receiver
22—Drive for Propane Compressor
23—Propane Refrigerant Expansion Valves

mine the volatility of the gases and it is therefore obvious that they should be held constant.

The separation of hydrocarbon constituents requires low temperatures or high pressures in the columns. It is well known that the principals of proper separation require that equilibrium between the gases and the liquids should be maintained through the height of the separation column. Inasmuch as all gases may be liquefied at common temperatures when there is pressure available, this means that ethane, propylene, propane, butylene, butane, ethylene may be separated by fractionation, whereas methane requires unusually low temperatures and high pressures when it is to be extracted. In the design of the separation columns it has been found that the most economical operating pressures are the lower ones that assure gaseous and liquid equilibrium at the uppermost plate in the separation column.

SEPARATION COLUMNS

There are various controlling factors that determine the details and construction of the separation column for ethylene extraction plants. Of the two types of columns the plate column is the most suitable due to ease of control, excellent contact between gas and liquid; minor variations of internal conditions are more easily absorbed by the liquid on each plate, and finally more accurate separation per unit dimension of the vertical height.

To effect better separation of the ethylene from the other constituents, it has been found that two columns are desirable. Allowance should be made for collecting the gas which leaves the cracking coil furnace in order to prevent unusual fluctuations. This is readily accomplished by introducing a suitable gas accumulator. The gas leaving the cracking coil is collected by this accumulator, from which the suction is taken by a gas compressor. The pressure is raised to at least 10 atmospheres and should then be discharged through a water-cooled condenser which extracts the heat of compression and lowers the temperature several degrees above the available cooling water temperature. After passing through this cooler the gas is discharged midway up the first separation column, which is termed as the methane column. This methane column contains 30 plates of an approved design, which eliminate all saturated constituents. All of the heavy constituents, including ethylene are separated as a bottom product, which are discharged into a run-down tank operating at the same pressure as the methane column. A run-down tank is a very essential device, as it serves as a surge reservoir for the second separation column. A suitable reboiler is introduced in the base of the methane column for reboiling of fractionated liquids.

The stripped gas leaves the top of the column and is conveyed through a direct expansion cooled condenser by a gas compressor and is discharged at a pressure of 70 atmospheres into a reflux separator. The stripped gas that leaves the top of the first column consists of hydrogen, methane, and some ethylene. The pressure in the methane column is slightly above 30 atmospheres and the temperature of the top plate is maintained by direct expansion at minus 40°F. In the reflux separator vapors remain uncondensed and are discharged from the system by proper automatic control equipment, while the condensed reflux is returned to the top of the methane column.

The second, or ethane column operates at 20 atmospheres, and this too is equipped with similar

TABLE 1
Thermodynamic Properties of Ethylene

Temp. Deg. F. t	Temp. Deg. C. t	Pressure In Lbs. Per Sq. In.		Specific Volume Cu. Ft. Per Lb.		Density Lbs. Per Cu. Ft.		Heat Content B.T.U. Per Lb.		Latent Heat B.T.U. Per Lb. L	Entropy B.T.U. Per Lb. Per Deg F.	
		Absolute P	Gage gP	Liquid v	Vapor V	Liquid 1/v	Vapor 1/V	Liquid h	Vapor H		Liquid s	Vapor S
—176.8	—116	6.75	*16.18	0.02732	16.4	36.60	0.061	0	213.9	213.9	0.000	0.756
—173.2	—114	7.72	*14.21	0.02746	14.5	36.42	0.069	1.8	214.5	212.7	0.006	0.749
—169.6	—112	8.80	*12.01	0.02760	12.7	36.23	0.079	3.5	215.1	211.6	0.012	0.742
—166.0	—110	10.00	* 9.57	0.02774	11.1	36.05	0.090	5.3	215.8	210.5	0.018	0.735
—162.4	—108	11.35	* 7.02	0.02788	9.71	35.87	0.103	7.1	216.3	209.2	0.024	0.728
—158.8	—106	12.80	* 3.87	0.02802	8.62	35.69	0.116	9.0	216.9	207.9	0.030	0.722
—155.2	—104	14.44	* 0.52	0.02815	7.52	35.51	0.131	10.8	217.5	206.7	0.036	0.716
—151.6	—102	16.22	1.52	0.02830	6.76	35.32	0.148	12.6	218.1	205.5	0.042	0.710
—148.0	—100	18.17	3.47	0.02846	6.06	35.14	0.165	14.5	218.7	204.2	0.048	0.704
—144.4	— 98	20.36	5.66	0.02860	5.49	34.96	0.182	16.4	219.2	202.8	0.054	0.698
—140.8	— 96	22.65	7.95	0.02875	4.98	34.78	0.201	18.3	219.9	201.6	0.060	0.693
—137.2	— 94	25.17	10.47	0.02890	4.50	34.60	0.222	20.2	220.6	200.4	0.066	0.688
—133.6	— 92	27.91	13.21	0.02905	4.08	34.42	0.245	22.2	221.2	199.0	0.072	0.683
—130.0	— 90	30.86	16.16	0.02921	3.72	34.23	0.269	24.1	221.8	197.7	0.078	0.678
—126.4	— 88	34.06	19.36	0.02937	3.39	34.05	0.295	26.0	222.3	196.3	0.084	0.673
—122.8	— 86	37.50	22.80	0.02953	3.11	33.87	0.322	28.1	223.1	195.0	0.090	0.669
—119.2	— 84	41.19	26.49	0.02968	2.85	33.69	0.351	30.1	223.8	193.7	0.096	0.665
—115.6	— 82	45.16	30.46	0.02985	2.62	33.50	0.382	32.2	224.6	192.4	0.102	0.661
—112.0	— 80	49.40	34.70	0.03003	2.40	33.30	0.416	34.2	225.3	191.1	0.108	0.658
—108.4	— 78	53.93	39.23	0.03020	2.21	33.11	0.452	36.3	226.0	189.7	0.114	0.654
—104.8	— 76	58.76	44.06	0.03039	2.04	32.91	0.490	38.4	226.7	188.3	0.120	0.650
—101.2	— 74	63.90	49.20	0.03056	1.89	32.72	0.530	40.5	227.3	186.8	0.125	0.647
— 97.6	— 72	69.37	54.67	0.03077	1.75	32.50	0.573	42.6	228.0	185.4	0.131	0.643
— 94.0	— 70	75.17	60.47	0.03098	1.62	32.28	0.617	44.8	228.7	183.9	0.137	0.640
— 90.4	— 68	81.32	66.62	0.03118	1.51	32.07	0.663	47.0	229.4	182.4	0.143	0.637
— 86.8	— 66	87.88	73.18	0.03139	1.40	31.86	0.713	49.2	230.1	180.9	0.149	0.634
— 83.2	— 64	94.76	80.06	0.03161	1.31	31.64	0.765	51.4	230.8	179.4	0.155	0.631
— 79.6	— 62	102.0	87.3	0.03183	1.22	31.42	0.820	53.7	231.5	177.8	0.161	0.628
— 76.0	— 60	109.7	95.0	0.03205	1.14	31.20	0.877	55.9	232.1	176.2	0.166	0.626
— 72.4	— 58	117.7	103.0	0.03228	1.07	30.98	0.938	58.3	232.9	174.6	0.172	0.623
— 68.8	— 56	126.2	111.5	0.03251	1.00	30.76	0.999	60.6	233.5	172.9	0.178	0.621
— 65.2	— 54	135.1	120.4	0.03274	0.935	30.54	1.065	63.0	234.3	171.3	0.184	0.618
— 61.6	— 52	144.4	129.7	0.03299	0.885	30.31	1.138	65.3	234.9	169.5	0.100	0.616
— 58.0	— 50	154.2	139.5	0.03326	0.826	30.07	1.212	67.8	235.5	167.7	0.196	0.613
— 54.4	— 48	164.5	149.8	0.03352	0.775	29.83	1.292	70.3	235.8	165.5	0.202	0.610
— 50.8	— 46	175.2	160.5	0.03381	0.730	29.58	1.374	72.7	236.1	163.4	0.208	0.608
— 47.2	— 44	186.7	172.0	0.03408	0.685	29.34	1.460	75.3	236.4	161.2	0.214	0.605
— 43.6	— 42	198.1	183.4	0.03436	0.645	29.10	1.552	77.8	236.7	158.9	0.220	0.602
— 40.0	— 40	210.4	196.7	0.03467	0.606	28.84	1.649	80.4	237.0	156.6	0.226	0.599
— 36.4	— 38	223.2	208.5	0.03499	0.571	28.58	1.754	83.0	237.3	154.3	0.232	0.596
— 32.8	— 36	236.6	221.9	0.03531	0.535	28.32	1.865	85.7	237.5	151.8	0.238	0.594
— 29.2	— 34	250.5	235.8	0.03566	0.503	28.04	1.985	88.4	237.4	149.0	0.244	0.590
— 25.8	— 32	265.2	250.5	0.03602	0.474	27.76	2.11	91.1	237.4	146.3	0.250	0.587
— 22.0	— 30	280.1	265.4	0.03640	0.444	27.47	2.25	93.9	237.4	143.5	0.256	0.584
— 18.4	— 28	296.0	281.3	0.03679	0.418	27.18	2.39	96.8	237.2	140.4	0.263	0.581
— 14.8	— 26	312.2	297.5	0.03721	0.392	26.87	2.55	99.6	236.8	137.1	0.269	0.577
— 11.2	— 24	329.3	314.6	0.03760	0.368	26.56	2.72	102.7	236.4	133.7	0.275	0.573
— 7.6	— 22	346.8	332.1	0.03811	0.345	26.24	2.90	105.7	235.9	130.2	0.282	0.570
— 4.0	— 20	365.5	350.8	0.03858	0.323	25.92	3.10	108.8	235.3	126.5	0.288	0.566
— 0.4	— 18	384.3	369.6	0.03911	0.302	25.57	3.31	112.0	234.8	122.8	0.295	0.562
+ 3.2	— 16	404.4	389.7	0.03965	0.283	25.22	3.53	115.2	234.2	118.9	0.301	0.558
6.8	— 14	424.7	410.0	0.04026	0.266	24.84	3.76	118.7	233.6	114.9	0.308	0.555
10.4	— 12	446.5	431.8	0.04090	0.249	24.45	4.01	122.3	233.0	110.6	0.316	0.551
14.0	— 10	468.7	454.0	0.04161	0.234	24.03	4.28	126.0	232.4	106.5	0.323	0.548
17.6	— 8	491.8	477.1	0.04237	0.218	23.60	4.58	130	232	101.9	0.331	0.545
21.2	— 6	515.0	500.3	0.04323	0.205	23.13	4.88	134	230	97.0	0.339	0.541
24.8	— 4	540.4	525.7	0.04419	0.190	22.63	5.26	138	229	91.9	0.348	0.537
28.4	— 2	656.7	551.0	0.04527	0.176	22.09	5.68	142	228	86.0	0.357	0.533
32.0	0	593.3	578.6	0.04651	0.163	21.48	6.15	147	226	79.5	0.367	0.529
35.6	+ 2	619.8	606.1	0.04801	0.149	20.83	6.70	152	224	72.3	0.377	0.523
39.2	4	649.5	635.1	0.04990	0.135	20.04	7.39	158	222	63.6	0.389	0.520
42.8	6	678.0	664.3	0.05230	0.121	19.12	8.27	166	218	52.0	0.404	0.508
46.4	8	710.3	695.6	0.05580	0.103	17.92	9.68	177	211	34.5	0.420	0.494
†48.85	9.36	731.8	717.1	0.07418	0.074	13.48	13.48	194	194	0	0.460	0.460

*Inches of Mercury below one standard atmosphere (29.92″). †Critical.

plates as the methane column. The ethylene and other heavy constituents collected in the run-down tank are passed to the ethane column mid-way up, by the liquid level flow control, which controls the pressure differential. In this column the required ethylene product is separated by fractionation as an overhead product.

The residual hydrocarbons are delivered as a bottom product at a temperature of 90°F. to the gas stripping column to be used as a recycle reflux. The heat liberated from the residual hydrocarbons is utilized in the reboiler of the first column. In the base of the ethane column is provided a steam heated reboiler. The steam utilized is admitted through a suitable control valve, which is thermostatically actuated from the gas inlet temperature. The overhead product from the ethane column together with the vaporized reflux passes through a cooler that is cooled by means of direct expansion which removes sufficient heat to condense the necessary amount of reflux for this column. The reflux is returned to the top of the ethane column by means of a close clearance pump thermostatically controlled by the outlet temperature of vapor from the top of the column. The uncondensed overhead product from the reflux separator is the finished 98 per cent pure ethylene.

REFRIGERATION PLANT

The choice of the refrigerant to be used for any industrial process must always be selected by the specific conditions to be encountered. A refrigerant cannot be used if the temperature of the available cooling water lies above the critical temperature of that refrigerant. Ammonia is of course the most common refrigerant in use, however, due to the necessity of operating under high vacuum conditions when the temperature of the evaporating units are low, its toxic characteristics and contamination due to interleakage excludes its use in ethylene plants. A hydrocarbon refrigerant such as propane, which has very nearly similar vapor pressures should be used. Only refrigerants that have the lowest chemical reactivity, lowest corrosive actions on metals should be used. Table 2 gives comparable vapor pressures for the various hydrocarbon refrigerants that should be used in connection with ethylene plants. It will be observed that the lowest temperature in the methane column previously discussed was minus 40°F. A split of at least 10 degrees should be allowed between the evaporating temperature and the refrigerant, thus making the temperature of the refrigerant minus 50°F. The table shows that at this temperature the vapor pressure for Propane will be 4.3 inches of mercury below one standard atmosphere, while that for Ammonia will be 14.3 inches of mercury. Since the temperature of the available cooling water for the refrigerant condenser will be 70°F. inlet and 80°F. outlet, the temperature of the outlet refrigerant from the condenser should be under 90°F. For this temperature the vapor pressure of propane will be 149 pounds gauge, as against that of ammonia of 165.9 pounds gage. The accompanying table of refrigerants will be useful to engineers

TABLE 2

Pressures of Hydrocarbon Refrigerants Comparable to Ammonia and Carbon Dioxide—Gauge Pressures

°F. Temperature	Ammonia	Carbon Dioxide	Ethane	Propane	Butane	Isobutane	Ethylene
—160	.....	.....	.....	.....	.....	.....	* 4.0
—140	.....	.....	* 10.1	.....	.....	.....	7.9
—120	.....	.....	4.0	.....	.....	.....	26.5
—110	.....	0	9.0	.....	.....	.....	36.0
—100	*27.4	7.5	15.0	.....	.....	.....	49.2
— 90	*26.1	19.2	24.9	.....	.....	.....	66.6
— 80	*24.3	36.1	35.0	.....	.....	.....	85.0
— 70	*21.9	60.1	45.0	*14.9	.....	.....	106.0
— 60	*18.6	80.0	60.0	*10.1	.....	.....	129.0
— 50	*14.3	103.2	77.6	* 4.3	.....	.....	160.5
— 40	* 8.7	131.0	98.2	1.5	.....	.....	195.7
— 30	* 1.6	163.0	120.3	5.6	.....	.....	235.0
— 20	3.6	205.8	144.8	10.7	.....	* 14.6	275.0
— 10	9.0	247.0	172.0	16.7	.....	* 11.0	320.0
0	15.7	293.9	204.0	23.5	* 15.0	* 6.3	370.0
+ 20	33.5	407.3	277.0	40.8	* 6.3	3.5	500.0
+ 40	58.6	550.7	368.0	63.3	3.0	12.2	650.0
+ 60	92.9	729.5	466.0	92.4	11.6	24.0	.....
+ 80	138.3	949.6	610.0	128.1	22.9	39.2	.....
+ 90	165.9	1080.0	703.0	149.0	.....	.....	.....
+100	197.2	.....	.....	172.0	37.5	59.0	.....
+125	293.1	.....	.....	239.0	61.3	90.1	.....
+150	.....	.....	.....	.....	.....	.....	.....
+200	.....	.....	.....	.....	.....	.....	.....

*Inches of Mercury below one standard atmosphere.

in determining which refrigerant will be most economical to use.

ETHYLENE PLANT CONTROLS

In the design of an ethylene plant, great stress should be laid upon the accuracy of the control equipment. The operator of an ethylene plant usually does not know when close separation is being obtained. The common methods of testing the vapor tension leave much uncertainty. Uniform plant operation depends upon proper control equipment and if was possible to have a feed stock of unvarying constituency the design of the separation columns would be very simple indeed. With the proper automatic controls, temperature controls and steam regulators the result will be a product that will be constant over consecutive periods of operation throughout the cycle and less operators will be needed to operate the ethylene plant.

ESTIMATED COST

It was previously stated that to make an ethylene plant an attractive investment the ethylene should be produced at a total cost of under six cents per pound, which should include raw materials, yields, operating costs, and fixed charges. In reference to the yields, the ethylene plant should have a relatively high efficiency when the percentage of plant yield will be low. The following costs are given for a plant that will produce 98 per cent pure ethylene, which will be free of sulphur or acetylenes.

Operating Costs	Cost Per Day
Raw materials	$250.00
Steam consumption	10.80
Electricity	60.00
Condenser water	20.00
Fuel oil	10.00
Labor	40.00
Maintenance	2.00
Total Operating Costs	$394.00
Fixed Charges	
Depreciation of plant	$30.00
Taxes	5.00
Insurance	2.00
Interest on investment	10.00
Lease on plant site	8.00
Total Fixed Charges	$ 55.00
Total Cost Per Day	$449.00

Total Cost Per Year $449.00 × 365 days—$162,885.00

(Assume plant is closed down for two weeks for cleaning). Plant will produce 11,000 pounds per day × (365—14) = 3,861,000 pounds of ethylene per year. Then;

$$\text{Cost to make ethylene} = \frac{\$162{,}885.00}{3{,}861{,}000 \text{ lbs.}} = \$.046 \text{ per lb.}$$

Improvements *in* Solvent Refining Of Lubricating Oils

By the Edeleanu Process

WALTER KAIN
Edeleanu Company, Ltd.

THROUGH use of liquid sulphur dioxide and benzol, in varying proportions to suit various oils, the scope of application of the Edeleanu process has been materially enlarged. In this article, Dr. Walter Kain discusses the application of the Edeleanu process using SO_2 as the solvent and the modified Edeleanu process employing SO_2 and benzol. The fundamental importance of this development lies in the greatly improved results obtainable through the use of the new double solvent without any major changes in the method of operation of the process.

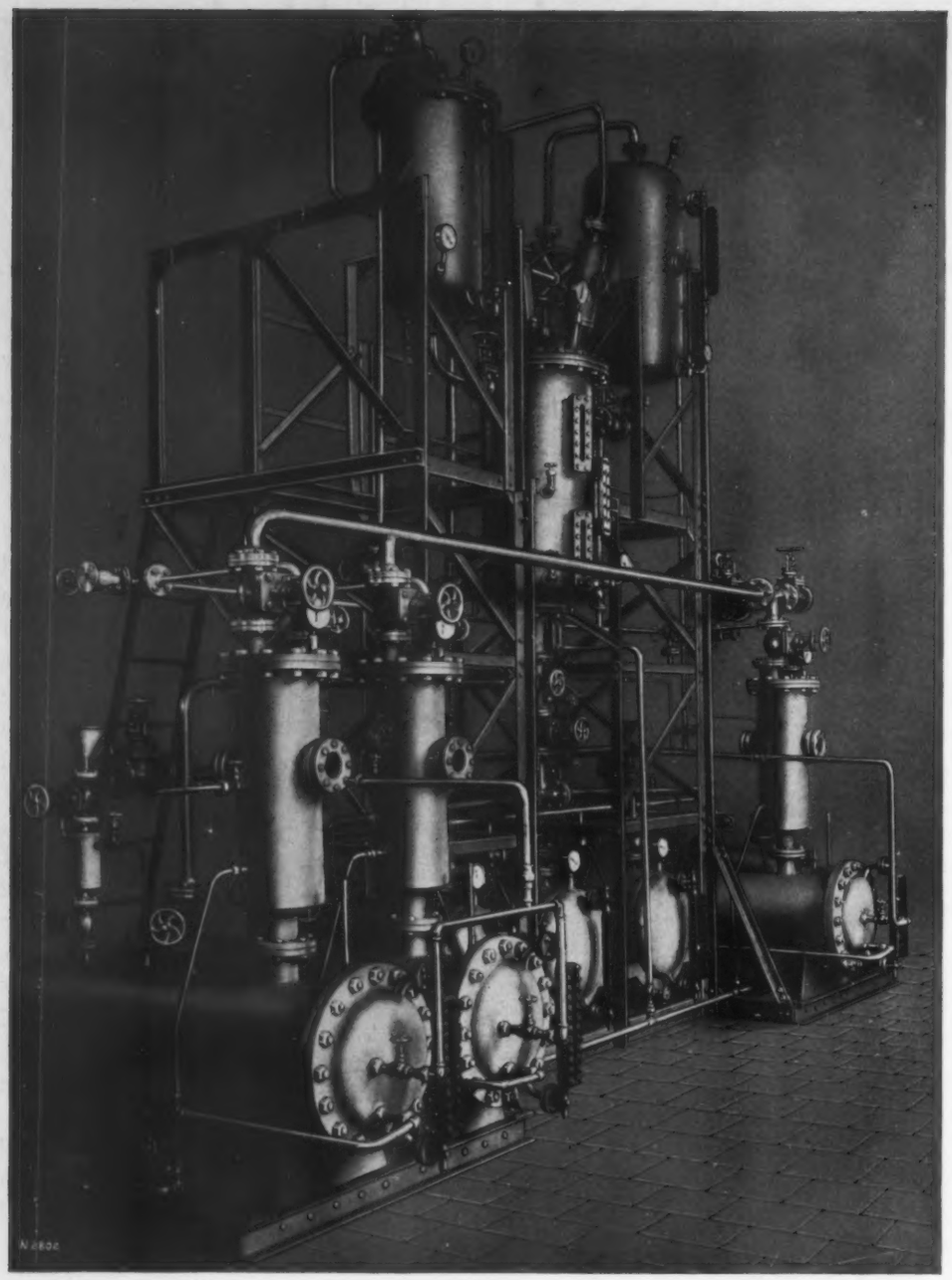
THE general principles of the Edeleanu refining process are well known to most petroleum refiners. It is less generally known, however, that the process is not limited to the treatment of light oils, such as kerosene and gasoline, but that the process is also used on a large scale for treating lubricating oils. In the following an outline shall be given of the effects of SO_2 treatment on various lubricating oil fractions and how the scope and flexibility of the process has been increased by recent developments.

The action of liquid sulphur dioxide on lubricating oils is essentially the same as it is on kerosene. The refining effect is chiefly of a physical nature, the liquid sulphur dioxide acting as a selective solvent. As to the question of what may be accomplished through treatment of lubricating oils with liquid sulphur dioxide, reference is made to Table No. 1, showing the results of Edeleanu treatment on a large variety of lubricating stocks. Glancing at the table it becomes immediately apparent that the process is of beneficial effect on all stocks, and that the end-product of the process, the so-called raffinate, is an oil of greatly improved quality over the corresponding charging stock. Regardless of the type or origin of the petroleum stock, and regardless of whether distillates or residual oils are treated, treatment with liquid sulphur dioxide results in a refined lubricating oil of higher gravity, lower Conradson test and of a flatter viscosity curve. While an improvement may be observed in every case, the degree of improvement as well as the yield of raffinate varies greatly and depends on the type of the charging stock.

This is entirely in line with the selective action of liquid sulphur dioxide toward the various groups of hydrocarbons. As is well known, paraffine and naphthene hydrocarbons are not, or only very little, soluble in liquid SO_2 at low temperature, while aromatic and unsaturated hydrocarbons are soluble at any temperature. Lubricating oil stocks containing large amounts of aromatics and unsaturates are therefore more drastically refined by treatment with liquid SO_2 than are oils of paraffinic character. On the other hand, the more aromatics and unsaturates an oil contains, the lower will be the yield of refined oil. In line with this it may be seen from Table No. 1 that the most drastic refining effects and, simultaneously, the lowest yields of raffinate are obtained from California oils and that comparatively small refining effects but high yields of raffinate result from the treatment of Pennsylvania stocks.

Very interesting and favorable results are obtained with Edeleanu treatment of light lubricating stocks, such as transformer and turbine oils. Edeleanu refined transformer oils are known to have a very low tendency to form sludge. The SO_2 refining process represents, furthermore, an ideal method for obtaining a good "Life Test" (developed by General Electric Company). The treatment of transformer stocks is carried out preferably in such a manner that the Edeleanu raffinates are obtained. With sulphuric acid treatment it is frequently impossible to reach even the required minimum Life Test of 21 days. An interesting discovery was made showing that after treatment of Edeleanu oil raffinates with sulphuric acid does not improve, but is actually detrimental to the Life Test. This may be seen from the following examples:

A California transformer oil distillate of 57 Visc. at 100° F. was Edeleanu treated and the raffinate was neutralized and filtered, whereby a Life Test of over 40 days could be obtained. Another method was then tried out by aftertreating the same raffinate with 10 pounds of 98 per cent sulphuric acid per barrel, and then neutralized and filtered in the same manner as



Experimental Plant for carrying out the Edeleanu Process

above, but this resulted in a Life Test of only nine days. Still more unfavorable results were obtained upon aftertreatment of the raffinate with 30 pounds of 98 per cent sulphuric acid and neutralization and filtration as well as upon aftertreatment with 10 pounds of 98 per cent sulphuric acid and 60 pounds of oleum per barrel and neutralizing plus filtering. The finished oils of both treatments gave Life Tests of only four days.

The same tendency is observed on Gulf Coast transformer oils: Refining with sulphuric acid results in very poor Life Tests, while tests of over 30 days are obtained upon treatment with SO_2 followed by neutralization and filtration.

Numerous tests have shown that Edeleanu treated transformer oils have proved to be more resistant to oxidation, than the oils given the usual sulphuric acid treatment, and that refining losses are smaller. From a practical point of view, the application of the Edeleanu process should be of great advantage in all cases where the usual refining methods fail to bring the transformer oil up to certain required specifications.

Extensive studies have been made on Edeleanu treated turbine oils. Long duration tests on laboratory and industrial scale carried out by well known authorities clearly indicate that sulphuric acid treated oils deteriorate much faster than SO_2 treated oils do, the tendency toward oxidation being much smaller with the latter. Special attention was paid to such important factors as change in gravity and viscosity, and tests as Tar Number (Kissling method) Tar Forming Number, Acid Number, etc., and in almost all cases Edeleanu refined oils proved to be of greater stability.

One test was carried out in which a sulphuric acid

and a liquid sulphur dioxide refined oil (both from the same crude) were both subjected to the same operating conditions. The test was extended over a period of one year for the acid refined oil and two years for the Edeleanu refined oil. The trial run with the acid refined oil was of necessity discontinued on account of a fine gray sludge which was found in all parts of the oil system. Both oils were checked in regular intervals and all data and observations were noted carefully. In spite of the difficulties connected with such comparative tests, the available data showed clearly that the rise in specific gravity, viscosity, acid number, tar number and tar forming number of the Edeleanu treated oil proceeded at a much slower pace than that of the sulphuric acid treated oil. The results obtained indicate clearly the advantages which may be expected from Edeleanu treated turbine oils in actual service. Other comparative tests demonstrated that by means of refining with liquid sulphur dioxide, even turbine oils from lower type crude, such as certain Venezuelan oils, may be converted into high class finished products without excessive losses.

As with light lubricating oils, the stability factor is the strongest argument in favor of the Edeleanu process with heavier stocks. It is the selective solvent action of the liquid sulphur dioxide that causes the extraction of the substances which are most susceptible to oxidation and decomposition during service. In many cases the application of even great amounts of sulphuric acid do not equal the results obtained from treatment with liquid sulphur dioxide. The result of the usual laboratory tests, such as gravity, temperature-viscosity curve, Conradson test, etc., may be seen from Table No. 1, but these tests show only partly what SO_2 will accomplish. Better indications as to the suitability of SO_2 refined oils are offered by such tests in which the oil—over a period of time—is subjected to conditions actually prevailing during service. The claims as to the stability of Edeleanu treated oils have been checked and verified by the Sligh and other accelerated oxidation tests, block motor tests, and by such tests as the U. S. Navy Bearing Test. The excellent performance of SO_2 refined lubricating oils in the Navy Bearing Test machine is specially remarkable. It may, therefore, safely be said that treatment with liquid SO_2 tends to produce lubricating oils which will measure up to the most modern requirements and testing methods.

During the last few years the standard of lubricating oils have been raised steadily in the United States, due mainly to modern requirements of the automobile industry. Petroleum refiners have tried to find means and ways of producing higher grade motor oils from their crudes. The tendency is to produce oils able to withstand bearing pressure in high compression motors, and of highest possible resistance towards oxidation. All refiners are trying to bring their oils up to these modern requirements and in this direction the Edeleanu process proved to be highly efficient. Edeleanu treated motor oils are successfully marketed on a large scale by several companies. In some cases, however, the action of SO_2 treatment, while working in the right direction, was not quite sufficient. This was felt mainly on certain types of heavy Mid-Continent oils. An after-treatment with sulphuric acid became necessary. The effect obtained by the combined SO_2 and acid treatment resulted in finished oils of higher quality than can

Extract Evaporators, Gas Coolers, Compressor and Vacuum Pumps in large commercial Edeleanu Unit.

TABLE NO. 1

Results Obtained Upon Subjecting Lubricating Oil Stocks to Liquid SO_2 Treatment

TYPE OF OIL TREATED	Gravity (A.P.I.°) of Charging Stock	Viscosity at 100° F. of Charging Stock	Viscosity at 200° F. of Charging Stock	Viscosity Index of Charging Stock	Conradson Carbon of Charging Stock in %	Amount of Liquid SO_2 used (counter-current)	Temp. of Treat-ment °F	Gravity (A.P.I.) of Raffinate	Viscosity of Raffinate at 100° F.	Viscosity of Raffinate at 210° F.	Viscosity Index of Raffinate	Conradson Carbon of Raffinate in %	Raff. Yield (by vol.)	Extract Yield (by vol.)
California Distillate	15.8	3974	100	—91	0.32	200 vol%	14	21.0	1708	82	+1	0.29	68	32
California Distillate	15.3	2733	86	Below 0	0.51	200 vol%	25	21.2	1247	74	16	0.16	64	36
California Distillate	15.3	2733	86	Below 0	0.51	200 vol%	95	22.2	1143	74	31	0.13	52	48
Gulf Coast Distillate	20.8	915	66	23	0.24	200 vol%	25	23.7	673	63	53	0.11	84	16
New Mexico: 400 Viscosity	21.1	402	55	75	0.57	200 vol%	30	27.1	275	52	106	0.21	75	25
Midcontinent Vac. Overhead	21.6	....	178	69	3.06	250 vol%	32	23.8	....	153	84	1.97	92	8
Midcont. Resid. Undewaxed	21.4	....	154	74	4.5	225 vol%	32	23.4	....	145	93	3.5	92	8
Midcontinent Neutral	24.7	237	47	73	0.09	50 vol%	14	23.9	201	47	103	0.03	89	11
East Texas Neutral	25.5	208	46	81	0.07	100 vol%	32	23.9	175	45	98	0.03	82	18
Pennsylvania Bottom Cylinder Stock	26.2	1698	126	102	2.0	200 vol%	60	27.1	1532	123	106	1.8	97.5	2.5

be obtained by SO_2 or by sulphuric acid treatment alone. The following example will show how far the quality of an oil can be improved by the combined treatment:

A Mid-Continent cylinder stock of 20.5 A. P. I. and 2.8 per cent Conradson carbon test was first treated with liquid SO_2 resulting in a raffinate of 23.3 A. P. I. 1.7 per cent Conradson carbon and a viscosity index of 77. The SO_2 raffinate was then aftertreated with 10 pounds per barrel of sulphuric acid (98 per cent strength) and 12 per cent clay, yielding a finished product of 24.3 A. P. I. 1.1 per cent Conradson test and a Vis. Ind. of 80. It may still be added that the extract yield upon SO_2 treatment was 14.6 per cent, and that the sludge loss of the acid treatment amounted to 12.5 per cent.

The double treatment with SO_2 and sulphuric acid is advantageously applied in some cases but, generally, does not represent an ideal solution. The method involves additional expenses, which should be eliminated whenever possible. Apart from that, even the combined treatment does not lead to the desired results in all instances.

It became evident, therefore, that the conventional SO_2 refining process had to be modified in order to improve sufficiently certain types of heavy lubricating oils and to bring them up to the desired standard. Somewhat improved results were obtained when refining with increased amounts of liquid SO_2, and also when refining at higher temperatures, as may be seen from Table No. 1. The improvements, however, were in most cases too limited to come up to requirements. After much experimenting it was found that the most efficient as well as economical method to arrive at satisfactory results was to use as a refining agent, not straight liquid SO_2, but a mixture of benzol and liquid SO_2. The fundamental importance of this development lies in the greatly improved results obtainable through the use of the new double solvent without any major changes in the method of operation of the conventional Edeleanu process.

What the modified Edeleanu process, or the "SO_2-Benzol Process" can do, is shown in Table No. 2. The table has been made up in such a manner that the difference between straight SO_2 and SO_2-benzol treatment may be seen in each case. It may be said here that the results shown in Tables No. 1 and 2 refer to SO_2 and SO_2-benzol treatment exclusively without any aftertreatment. The reason for the more drastic refining

TABLE NO. 2

Treatment of Lubricating Oils With "SO_2-Benzol" vs straight SO_2

	I Gulf Coast Lubr. Oil Distillate				II California Lubr. Oil Distillate			III Midcontinent Untreated Neutral			IV East Texas Vac. Overhead* Cylinder Stock			V Midcontinent Vac. Overhead† Cylinder Stock		
	Untreated	200 vol% counter-current straight SO_2	200 vol% counter-current solvent consisting of 85% SO_2 and 15% benzol	200 vol% counter-current solvent consisting of 75% SO_2 and 25% benzol	Untreated	200 vol% counter-current straight SO_2	200 vol% counter-current solvent consisting of 75% SO_2 and 25% benzol	Untreated	200 vol% counter-current straight SO_2	200 vol% counter-current solvent consisting of 85% SO_2 and 15% benzol	Untreated	400 vol% counter-current straight SO_2	200 vol% counter-current solvent consisting of 60% SO_2 and 40% benzol	Untreated	250 vol% counter-current straight SO_2	250 vol% counter-current solvent consisting of 60% SO_2 and 40% benzol
Temp. of treatment	....	25°F	25°F	25°F	....	25°F	25°F	....	30°F	32°F	....	45°F	32°F	....	32°F	32°F
Gravity (A.P.I.°)	20.8	23.7	24.8	25.3	15.3	21.2	23.3	26.0	29.0	29.9	19.7	24.0	25.8	21.6	23.8	26.7
Viscosity at 100°F	915	673	615	570	2733	1247	967	298	247	237	....	....	....	....	....	....
Viscosity at 130°F	....	....	....	....	....	....	....	....	....	....	1380	763	586	1413	1032	691
Viscosity at 210°F	66	63	61.5	60.5	86	74	70	51	49	49	166	125	110	178	153	123
Viscosity Index	23	53	58	63	below 0	16	37	86	94	101	....	85	94	69	84	95.5
Conradson Carbon	0.24%	0.11%	0.08%	0.06%	0.5%	0.16%	0.07%	0.18%	0.10%	0.06%	3.5%	1.4%	0.9%	3.1%	2.0%	0.8%
Raffinate yield (by vol.)	....	84%	78%	74%	....	64%	48%	....	88%	83%	....	82%	62%	....	92%	71%

*Was dewaxed before treatment to 35°F pour point. Pour point of SO_2 raffinate was 40°F. Pour point of SO_2-benzol raffinate was 45°F.

†Distillate undewaxed, having pour point of 80°F.

effect obtained with the double solvent, is that the addition of benzol to the liquid sulphur dioxide causes a considerable increase of solution power and results in a more complete elimination of all undesirable substance. The proportion of benzol in the solvent mixture is important: An increased proportion of benzol results in a higher solution power of the solvent mixture and in better quality, but in a lower yield of the resulting raffinate. In practical operation a mixed solvent will be used, the benzol content of which will be between about 15 per cent to about 60 per cent of the total mixture. In the majority of cases the proportion of benzol will be below 50 per cent; in many instances, refining with a mixture containing 25 per cent benzol will prove to be sufficient. If the proportion of benzol is unduly high, the selectivity of the solvent mixture will increase; valuable hydrocarbons will pass into the extract layer, thereby reducing the yield of raffinate without a proportional improvement in quality of the refined oil. The type of oil under treatment, the desired quality of the finished product and economic considerations will determine the proportion of benzol to be used in each case. It is understood that in order to obtain uniform results the relation of liquid SO_2 to benzol must be kept constant during the treating period.

From Table No. 2 and from what has been said above, it is evident that the new SO_2-benzol method greatly increases the scope of the Edeleanu process. Previously, the process was limited to the use of straight liquid sulphur dioxide. Now, the type of treatment depends on the nature of the stock charged to the Edeleanu plant and on the results desired. In the case of light oils, including gasoline, kerosene and light lubricating oils, straight SO_2 treatment offers greater advantages. Wherever the application of straight SO_2 serves its purpose, refining with an SO_2-benzol mixture is unnecessary and cannot be suggested. Experiments with a large number of solvents have shown that liquid sulphur dioxide is unsurpassed as to its selectivity toward hydrocarbons. Straight liquid sulphur dioxide should therefore be applied in all cases where the quality of the resulting oils meets specifications. If, however, the refined oil does not come up to specifications, straight SO_2 treatment should be substituted by benzol-SO_2 treatment, the proportion of benzol depending on the desired quality of the finished product and on the extract loss which the respective oil can stand economically. The scope of the SO_2-benzol process is unusually large and the quality of an oil may be improved to a previously unknown extent. The difference between the characteristics of the charging stock and the refined products is such as to render the origin of an SO_2-benzol treated oil untraceable. An aftertreatment of SO_2-benzol treated oils with sulphuric acid is not necessary—except in very rare cases. The most suitable aftertreatment, if required, is clay treatment, or rerunning in presence of alkali.

As to the construction of SO_2-benzol treating plants, the plants do not differ very much from the old type Edeleanu units for lubricating oils of which a large number are successfully operating in the United States and abroad. Due to the difference in boiling points (liquid SO_2 at 14° F., benzol at 176° F., oil at above 600° F.), a practically complete and comparatively easy recovery of the liquid SO_2 and the benzol is rendered possible. The new type plant is constructed in such a way that refining may be accomplished with straight liquid SO_2 or with various proportions of a benzol-SO_2 mixture. A very high flexibility of operation is thus assured and the plant will prove to be of value under any market conditions and fit for an adequate treatment of any type of light or heavy petroleum stock.

Continuous Acid Treating of Light Oils in the Laboratory

E. W. ZUBLIN
Texas Pacific Coal and Oil Company

This paper was read before Thirteenth Annual Meeting, American Petroleum Institute, Houston, November 15, 1932.

A VAST amount of data has been accumulated in the past by many laboratories on the acid treating of gasolines and distillates with particular reference to cracked distillates. Treating in the laboratory is usually done by the batch method, presumably because of the simplicity of this operation. All that is required is a beaker, a stirrer and a separatory funnel; or if these requisites are not available a bottle and cork stopper will do as well.

Few investigators, if any, seem to have taken the trouble to devise a simple and effective continuous treating apparatus for laboratory use in spite of the well known fact that there can be, and usually are, wide differences between the results of treating tests as carried out by the batch or continuous method. Not only are the finished products likely to be different in regard to color, stability, octane number, etc., but also treating losses are apt to be of altogether different magnitudes. This is chiefly due to variations of the time element which in the case of continuous treatment is easily controlled, while in batch treating it is practically beyond control.

With the rapid advance of vapor phase cracking for the production of high octane number gasoline the difficulties of treating to chemically stabilize such gasolines have advanced at the same rate. There are produced today on a commercial scale cracked gasolines which can be stabilized by batch acid treatment at prohibitive losses only; but if this same gasoline or distillate is acid treated continuously treating losses are reasonable. A much smaller quantity of acid is required to achieve the same or better results. It is understood of course that acid treatment must be followed by sludge separation, neutralization with caustic or lime, and re-distillation with steam or under vacuum at a liquid temperature which should not exceed 300°F., or preferably 275°F.

The following example serves well to illustrate some of the differences that may occur upon acid treating a highly cracked distillate of 88 octane number by the two methods. The distillate in question had a 460°F. end point, was of a straw color, and was unstable in every respect. Batch acid treating tests were carried out at room temperature (75 to 80°F.) using from four to 15 pounds of sulphuric acid per barrel of distillate, the concentration of the acid ranging from 95 to 70 per cent. The minimum sludge loss was 15 per cent, not counting the loss by polymerization. The gasoline after neutralization and redistillation was in no case better than 20 color (Saybolt Colorimeter), had a high gum content and was unstable towards oxygen at 100 pounds pressure and 212°F.—the longest induction period was less than 90 minutes.

This same distillate was then treated continuou in the apparatus to be described, allowing an average time of contact of the acid with the oil of 60 seconds. Four pounds of 93½ per cent sulphuric acid caused a sludge loss of 4.6 per cent by volume and a polymerization loss of about two per cent. The color of the gasoline was 25+ after neutralization and redistillation, and was still 25+ after standing in a white glass bottle on an open shelf in the laboratory for eight months. The air-jet gum was 8. The induction period of the oxygen bomb test was better than four hours. The loss in octane number due to the acid treatment was two points. The temperature of the distillate going into the mixer was 80°F.; the temperature of the mixture leaving it was 140°F.

Sludge losses were calculated as follows: The rate of feed was determined before and after the test to insure that it remained constant. The amount of treated and sludge-free distillate that was being delivered for given time intervals was measured once the apparatus was going well. The following data are characteristic:

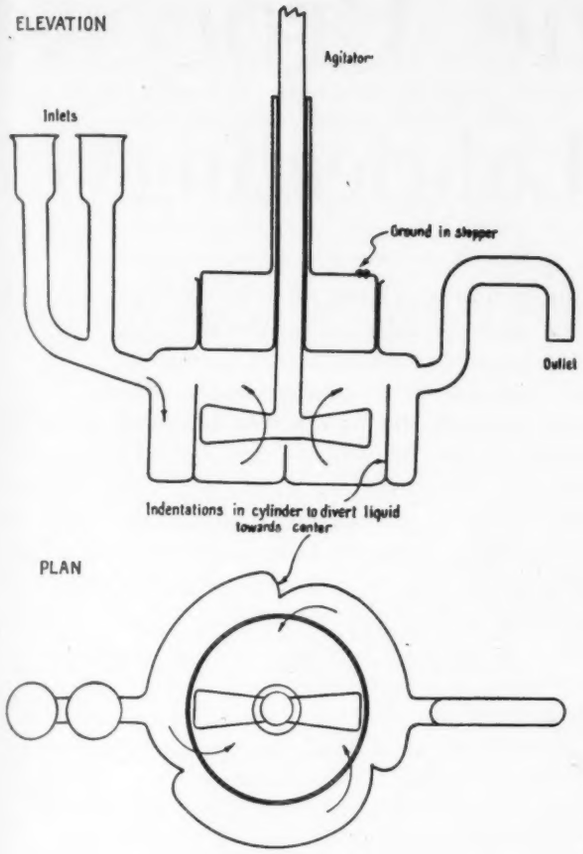
Rate of Feed Before Treat.....59.5 c.c. per Min.
Rate of Feed After Treat.....59.7 c.c. per Min.
Average Rate of Feed.....59.6 c.c. per Min.

Delivery of sludge-free distillate:		c.c.	c.c. per Min.
Interval	12 Min.	690	57.5
Interval	10 Min.	565	56.5
Interval	14 Min.	790	56.5
Interval	36 Min.	2,045	56.9

$$\text{Sludge Loss} = \frac{59.6 - 56.9}{59.6} \times 100 = 4.6\%$$

As will be seen from the accompanying sketches the main part of the apparatus consists of an agita-

Figure 1
Continuous Laboratory Agitator.



tor made of pyrex glass. A little air wheel moves the paddle stirrer which, if built properly, can be rotated at 2000 plus R.P.M. without danger of disruption. The stem of the stirrer protrudes through a ground-in glass stopper which carries a neck long enough to avoid loss from running over at this point. The intake of the agitator has two receiving arms, one for each fluid to be mixed. The outlet has the shape of a gooseneck so the agitator can be placed into a cooling or heating medium if desired.

The agitation vessel proper has a volume of 60 c.c. There are three dents in the side wall which throw the liquid towards the center once the agitator whirls it around. The paddles are arranged so the liquid is picked up through the center and is moved downward on the outside.

Fresh feed coming in is first forced down and then into the center. During this short passage it is already thoroughly mixed and chances are small that any particles may pass through the system insufficiently treated. To minimize this danger the outlet is placed immediately behind a dent so that in the immediate vicinity of the outlet high turbulence exists.

The dents, aside from acting as distributors, have the function of throwing the sludge or acid back into the distillate. The acid being heavier than the oil has a tendency to be thrown out centrifugally and to escape the whirling action of the paddle stirrer.

In Figure 2 the outlay of the entire treating system is shown. Gravity feed is used throughout. The feed is regulated and kept constant for hours by maintaining a constant differential between liquid level and feed nozzle. No valves or stop cocks are used to regulate the flow as this means invariably trouble due to fluctuations in the rate of feed.

The acid sludge in the mixture leaving the agitator can be partly settled in a settling vessel if desired. It is better though to run the entire mixture directly from the agitator into a bed of coarse clay such as, for instance, Olmstead clay. This type of clay has a remarkable retention capacity for the sludge and several quarts of treated distillate can be passed through a pound of clay before any sludge makes its appearance at the bottom outlet.

To ascertain whether the action of the clay was more than sludge removal several tests were carried out by running the mixture into laboratory centrifuge tubes. The sludge was removed by centrifuging and the distillate was neutralized with caustic and was redistilled as usual. The resulting gasoline was as stable as if the sludge had been removed by filtration through clay.

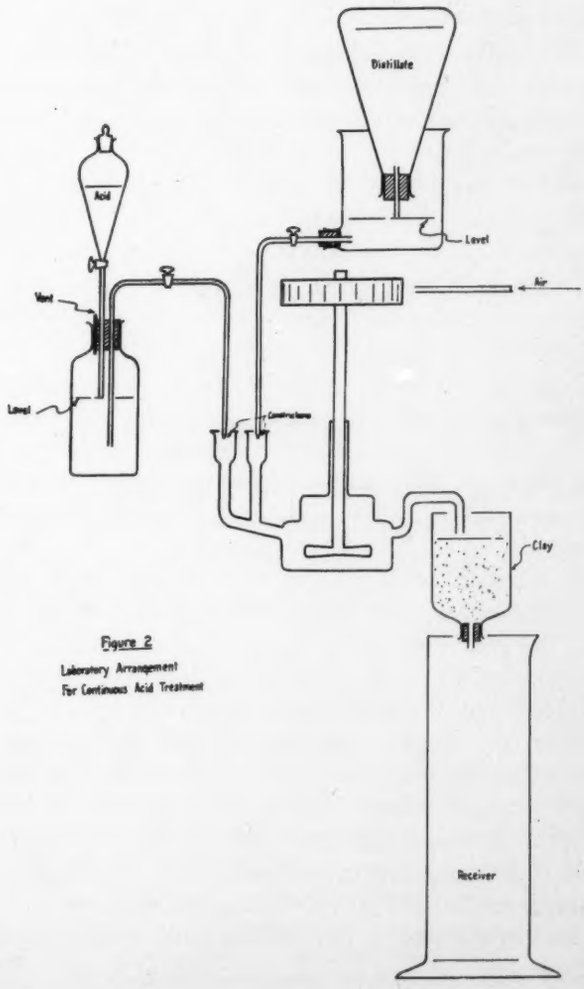


Figure 2
Laboratory Arrangement
For Continuous Acid Treatment

THE Nitrobenzene Process for Lubricating Oils

S. W. FERRIS and W. F. HOUGHTON
The Atlantic Refining Company

THE one requisite for a good motor oil upon which most authorities can agree is a flat viscosity-temperature slope, in order that proper protection against wear may be afforded at the high operating temperatures, without encountering such high viscosity at low temperatures that starting the engine becomes difficult. It is also agreed that the oil should be such that a minimum of carbon will be deposited in the cylinders, but there are wide differences of opinion as to the criteria upon which this property should be judged, some still putting their faith in the Conradson carbon value, while others agree with Bahlke, Barnard, Eisinger, and Fitz-Simons[1] that carbon deposition is largely a function of the boiling range of the oil, the presence of heavy ends being responsible for most of the difficulty.

Pennsylvania lubricating oils have long set the standard of quality because of their excellent viscosity-temperature relationships, in spite of the fact that they are admittedly poor with respect to carbon—whether this be based upon Conradson carbon or boiling range, for substantially all such motor oils contain the high boiling crude residuals.

Because Pennsylvania crudes are costly and of limited supply, some refiners have chosen to produce motor oils of reasonably good slope, either from residual or overhead material from Mid-Continent crudes; while others, neglecting slope and placing the emphasis upon carbon, have taken advantage of the high volatility and low cost of coastal crudes to prepare their motor oils by straight distillation methods.

A distillate motor oil from a Pennsylvania crude would possess, to a large extent, both advantages; but the yields would be cut down to such a marked degree that the cost would be prohibitive. Intensive efforts have, therefore, been made to produce lubricating oils of properties fundamentally better than the naturally occurring ones, and several processes have been developed which, to a greater or lesser degree, approach this goal. Some of these methods undertake actually to synthesize the lubricants, but it has been found that all crudes contain good as well as bad lubricants (even Pennsylvania crude contains components which are undesirable), and means have been discovered by which the desirable constituents may be separated, without chemical change, from the undesirable components. This paper deals with such a separation as effected by selective solvents, and especially by nitrobenzene,* which, after rather extended investigation, stands out as the most efficient selective solvent now commercially available.

The advantages of such a process are apparent. Instead of being forced to buy expensive crudes or to compromise with the quality of the lubricating oils, it is possible to employ cheap, plentiful crudes, or crudes purchased especially for the excellence of other fractions such as cracking stock, and yet economically produce lubricating oils of the quality desired, equalling or surpassing the Pennsylvania grade.

The advantage of an oil having a flat viscosity-temperature slope is illustrated in Figure 1, which shows the variation in viscosity over the normal temperature range for heavy motor oil (90 sec. Saybolt Universal viscosity at 210°F.) obtained from typical crudes. It is apparent that a given car, lubricated with the extreme Gulf Coast oil, would require a tremendously higher torque to start at 0°F. than would be the case if Pennsylvania oil were substituted. In fact, the former would require as much torque at 50°F. as would the latter at 0°F.

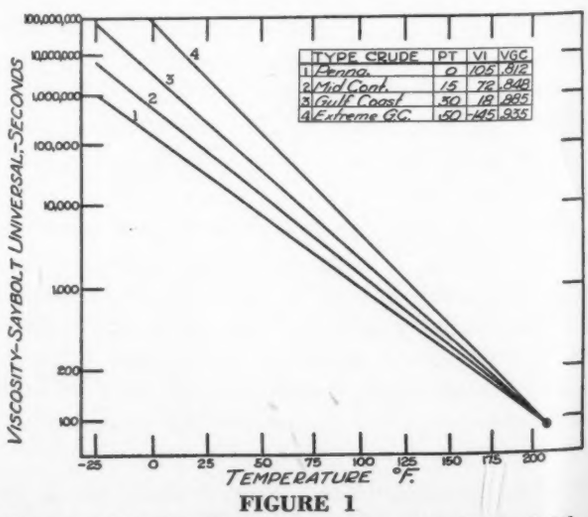


FIGURE 1
Range of Viscosity-Temperature Slopes for Natural Oils.

*U. S. Patent No. 1,788,569. Other patents pending.

LUBRICATING oils which combine the flat viscosity-temperature slopes of Pennsylvania products with the low carbon residue and short boiling range of Coastal distillates may be produced by means of the nitrobenzene extraction process.

Nitrobenzene is capable of handling a very wide range of lubricating stocks, either overhead or residual, from Coastal, mixed-base or paraffinic crudes, and separating therefrom lubricating stocks equal or superior to Pennsylvania. Oils of unusual properties for special purposes may also be readily prepared.

Nitrobenzene is the most satisfactory of all commercially available selective solvents from the point of view of selectivity and volume of solvents required. It is not easily contaminated, is stable under the conditions of operation, does not present unusual plant hazards, and is easily recovered. Stocks containing normal amounts of wax can be processed without difficulty. Operating costs are low, and the plant layout is free of complications.

This paper was presented at the Thirteenth Annual Meeting, American Petroleum Institute, at Houston, November 17, 1932.

MEASUREMENT OF PARAFFINICITY

Lubricating oils of low viscosity-temperature coefficient are usually referred to as "paraffinic," while those of rapid viscosity change are termed "naphthenic." The degree of paraffinicity may be quantitatively expressed by any one of three different methods.

The one most frequently employed in this paper is the "viscosity-gravity constant,"[2] a value based upon the fact that paraffinic oils exhibit, for a given viscosity, higher (A.P.I.) gravities than do naphthenic oils. A low value of this constant indicates a high degree of paraffinicity, natural oils varying from about 0.810 for Pennsylvania to about 0.940 for extreme Coastal types.

Use is also made of the "viscosity index,"[3] the values of which run opposite to the viscosity-gravity constant (V.G.C.)—Pennsylvania being about 100, with coastals as low as minus 200; and finally of the "parvis" temperature, the derivation of which has not been described, but which may be defined as that temperature (deg. F.) at which a given oil exhibits the same viscosity as that exhibited at 0°F. by a typical Pennsylvania oil whose viscosity at 210° F. is identical with that of the given oil. In other words, it expresses the quality of the oil in the same terms as were used in the example of the engine starting torques.

Both viscosity index and "parvis" temperature are based directly upon viscosity-temperature relationships. While the correlation between these values and viscosity-gravity constant is not particularly close when considering a number of oils of radically different types, such as synthetic oils compared to natural, it may be safely stated that, whenever the viscosity-gravity constant is improved by selective extraction of a given stock, there will be a corresponding betterment in viscosity index and "parvis" temperature. The table in Figure 1 correlates roughly the three scales of paraffinicity.

Alignment charts which facilitate the determination of the constants have been prepared for both the viscosity-gravity constant[4] and viscosity index.[5]

PROCESS OF SELECTIVE EXTRACTION

There are many substances with which mineral oils are miscible only to a limited extent; and, so far as is known, the naphthenic oils (or constituents of oils) are invariably more soluble than are the paraffinic oils. If then, one of these solvents be added to a lubricating stock in the proper proportions and at the proper temperature, two layers will be formed —one consisting of the major portion of the solvent, in which the more naphthenic constituents of the oil are dissolved, and the other of the undissolved oil, containing a relatively small amount of the solvent. If the two layers be separated, and the solvent removed from each, the undissolved portion (raffinate) will be found to be more paraffinic than the stock, by reason of the removal of the naphthenic constituents (extract).

Before proceeding with details of the nitrobenzene treatment it would be well to list the requirements of a selective solvent, and to indicate as briefly as possible why we believe nitrobenzene to be the most suitable material.

The necessary qualities of the solvent may be listed as:

1. Non-reactive with stocks under the conditions of the process.

2. Easily separable from the respective fractions, preferably by distillation.

3. Capable of effecting a sharp separation between paraffinic and naphthenic constituents.

4. Of such solvent power that a given separation

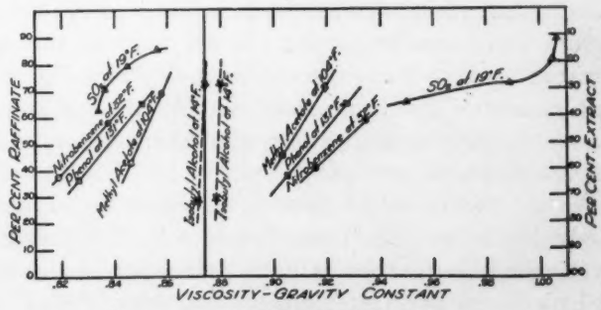


FIGURE 2
Comparison of Selective Solvents.
a. Efficiency of Separation.

may be made with reasonably small amounts of the solvent.

Figures 2 to 4 bear particularly upon the last two qualifications.

Five representative solvents have been selected for comparison, chosen from a much larger group which has been tested, many of which were reported in a previous publication.[6]

The properties of the stock employed follow:

Saybolt viscosity at 100°F., seconds	612
Saybolt viscosity at 210°F., seconds	57
Gravity, deg. A.P.I.	20.6
Viscosity-gravity constant (V.G.C.)	0.874
Viscosity index (V.I.)	19
"Parvis" temperature (P.T.), deg. F	29

Figure 2 demonstrates the efficiency of separation (item 3 above), regardless of the amount of solvent required. Each point represents a batch extraction

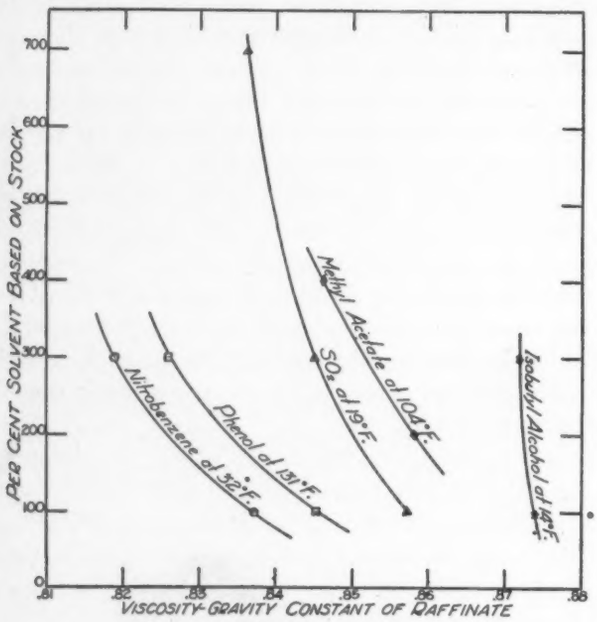


FIGURE 3

Comparison of Selective Solvents.
b. Volume Efficiency.

on the original stock, i.e., instead of applying more fresh solvent to a once-extracted fraction, a new extraction was made with a greater amount of solvent. The vertical line at V.G.C. = 0.874 represents the stock; the "per cent raffinate" scale at the left runs in a direction opposite to that of the "per cent extract" at the right, so that the two fractions resulting from a given run lie, within the accuracy of the experiment, upon the same horizontal line. For example, one of the treatments with liquid sulfur dioxide resulted in an 80 per cent raffinate of 0.845 V.G.C., and a 20 per cent extract of 1.05 V.G.C.

On this basis sulfur dioxide is shown to be definitely the most selective; it results in the greatest difference in properties between raffinate and extract, and gives the greatest yield of, say 0.840 V.G.C. It is apparent, however, that sulfur dioxide is incapable of producing a raffinate more paraffinic than about

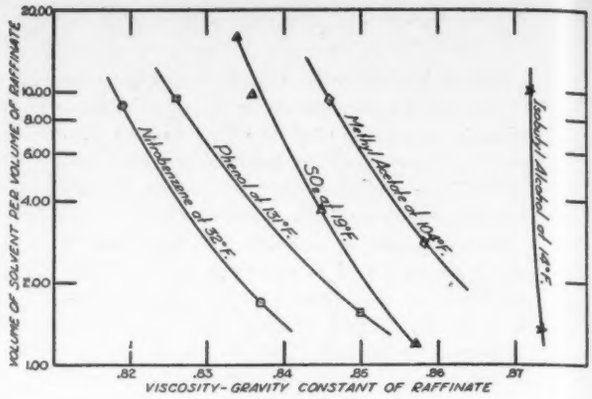

VOLUME OF SOLVENT PER VOLUME OF RAFFINATE
VISCOSITY-GRAVITY CONSTANT OF RAFFINATE
Nitrobenzene at 312°F.
Phenol at 131°F.
SO2 at 19°F.
Methyl Acetate at 104°F.
Isobutyl Alcohol at 147°F.

FIGURE 4

Comparison of Selective Solvents.
c. Over-all Efficiency.

0.830, whereas nitrobenzene or phenol can readily produce 0.815 (Pennsylvania quality) or better. Methyl acetate is also capable of 0.830 or thereabouts, while *iso*butyl alcohol merely producers two fractions of almost identical properties.

Figure 3 throws a somewhat different light upon the solvents, for it shows that even in the V.G.C. range, where all the solvents are applicable, there are required very much larger amounts of the other solvents than of phenol or nitrobenzene.

Figure 4 is essentially a combination of Figures 2 and 3. Since the amount of solvent required is directly reflected in the size of the equipment and the amount of heat required for solvent recovery, the relationships here shown may justly be considered highly important. The values in Table 1, taken from

TABLE 1
Comparison of Selective Solvents

Solvent	Volumes* of Solvent Required to Produce One Volume of Raffinate of V.G.C. of: 0.860	0.840	0.820
Nitrobenzene	0.5	1.4	8
Phenol	0.9	3.0	18
Sulfur dioxide	0.9	6.5	Impossible
Methyl acetate	2.3	21	Impossible
*Iso*butyl alcohol	Impossible	Impossible	Impossible

*By batch extraction.

Figure 4, may serve to emphasize the differences between these solvents.

Preliminary tests have been made on nearly 200 materials and exhaustive tests upon over 30 of the more promising. While a few were found—on the criteria just discussed—to be of efficiencies comparable with nitrobenzene, they were eliminated either on the score of poor stability or excessive cost.

TYPES OF EXTRACTION PROCEDURE

The results presented above were obtained by single batch extraction, as explained. There are at least three other methods of carrying out the extractions, each of which is more efficient than batch. It should be stated, however, that the efficiency of any solvent which we have investigated is increased, by

such methods, approximately in the same proportion. In other words, comparing solvents by extraction methods other than batch would not substantially alter the results with respect to efficiency from those presented above. The other methods are:

1. *Multiple extraction*: The raffinate from the first extraction is again treated with fresh solvent, etc.

2. *Batch counter-current*: Several treaters are employed, separations being effected in each, with the raffinate and extract layers being transferred—in opposite directions—from one treater to another. In effect, each bath of solvent is used as many times as there are treaters in the system; initially, upon raffinate about to be removed; finally, upon incoming stock.

3. *Continuous counter-current*: Solvent and stock pass counter-current through a tube or tower treater, being agitated during passage. Settling chambers are provided at each end to allow the phases to separate.

Before proceeding further it will be necessary to note a change in nomenclature. While "raffinate" and "extract" have been employed when several solvents were being considered, the remainder of the discussion will be confined principally to nitrobenzene, and the respective fractions will be referred to as "nitraffin" (raffinate) and "nitrene" (extract). The derivation of the terms is obvious from *nitro*benzene, para*ffin* and naphth*ene*.

Figures 5 and 6 illustrate the economies which may be effected over batch operation, the stock being the same as that in Figures 2 to 4. It will be noted (Figure 5) that multiple or batch counter-current treatment results in better yields of "nitraffin" of a given quality, the differences becoming proportionately greater as the quality of desired product becomes higher. Indeed, either of these methods is capable of producing material of a quality which would seem to be impossible with a single batch treatment. Still more striking advantages are found in the amount of solvent required (Figure 6), 0.810 V. G. C. being produced, for example, by only 100 per cent counter-current, whereas batch operation would require some 550 per cent.

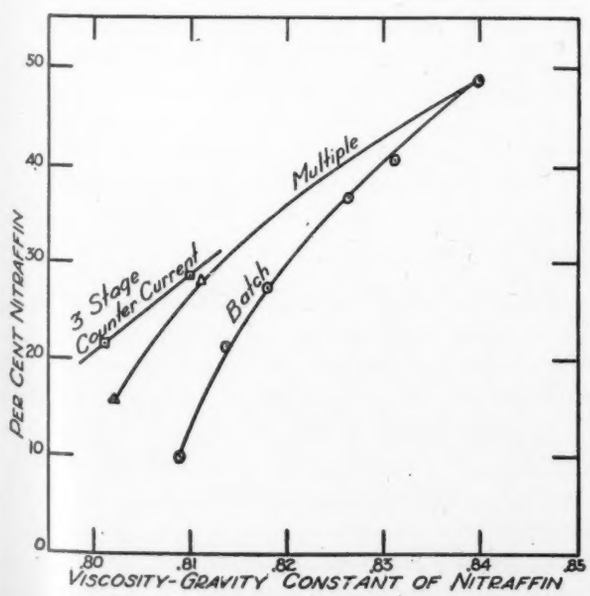


FIGURE 5
Comparison of Extraction Procedures.
a. "Nitraffin" Yield.

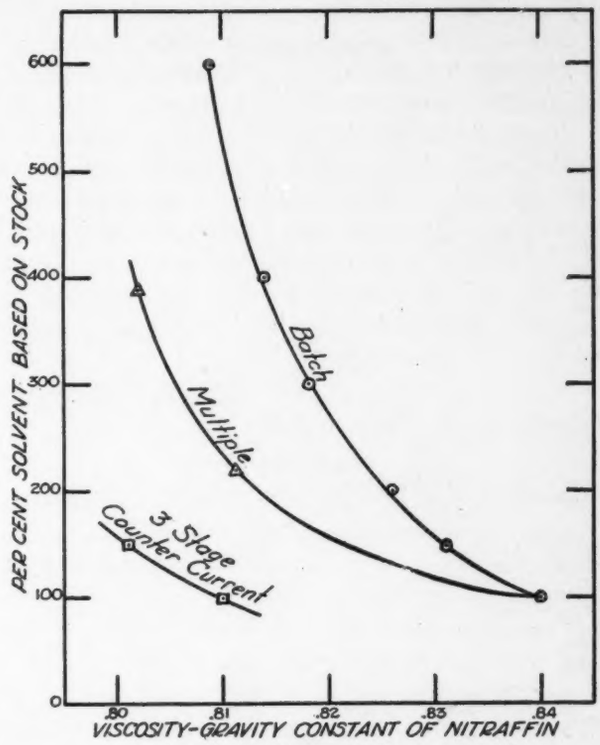


FIGURE 6
Comparison of Extraction Procedures.
b. Volume Efficiency.

Continuous counter-current treatment would yield results slightly superior, both in respect to yield and amount of solvent required, to three-stage counter-current. The differences are, however, not sufficient to demand such a procedure either in laboratory or plant. In the former, three-stage batch counter-current is ordinarily employed; in the latter, a provision is made for five stages (continuous), which represents even a closer approach to continuous counter-current.

EFFECT OF EXTRACTION TEMPERATURE

Temperature of extraction is a variable of which account must be taken. In general, any solvent will be inefficient unless it be employed at a temperature at least 40°F. below the miscibility temperature of stock and solvent. Further reduction in temperature effects the double result of decreasing the amount dissolved and increasing the selectivity of separation. In other words, it would appear disadvantageous in Figure 3, but advantageous in Figure 2. Happily for our efforts toward comparison, these opposite effects are approximately equal, resulting in little change in Figure 4.

With nitrobenzene the extraction temperatures

vary from a minimum of about 30°F. (for a naphthenic stock with low miscibility temperature) to perhaps 120°F. for a highly paraffinic stock. In five-stage counter-current extraction, the material being extracted obviously becomes more paraffinic as it approaches the "nitraffin" end where the fresh solvent is introduced, so that the temperature may be allowed to rise to a certain extent between the "nitrene" and "nitraffin" ends.

APPLICABLE STOCKS TO WHICH NITROBENZENE IS

In general, nitrobenzene may be applied to any petroleum stock which contains enough paraffinic material to produce a "nitraffin" layer, and whose boiling range is sufficiently high to allow separation and recovery of the solvent. This statement is predicated, of course, upon recovery by distillation; other methods, such as removal by washing, crystallizing or salting out, would somewhat broaden the range of stocks. Nitrobenzene boils, however, at about 410° F., so that it is readily separable by distillation from substantially all lubricating stocks.

TABLE 2
Variation in Viscosity of Charging Stock

Charge					
Saybolt Viscosity					
At 100 Deg. F.	At 210 Deg. F.	V.G.C.	Nitrobenzene Per Cent	"Nitraffin" Yield Per Cent	Finished Oil V.G.C.
152	...	0.844	120	30	0.804
305	...	0.853	100	49	0.811
612	...	0.874	150	22	0.801
...	77	0.856	125	53	0.810
...	178	0.863	150	52	0.812
...	275	0.895	150	21	0.798
...	379	0.861	250	26	0.813
...	632	0.888	100	40	0.806

TABLE 3
Variation in Paraffinicity of Charging Stock

Charge V.G.C.	Nitrobenzene Per Cent	"Nitraffin" Yield Per Cent	Finished Oil V.G.C.
0.895	100	20	0.803
0.880	125	33	0.802
0.874	150	22	0.801
0.864	100	41	0.810
0.857	200	41	0.807
0.844	120	30	0.804
0.817	60	74	0.801
0.808	50	80	0.800

Tables 2 to 5 list some of the stocks to which nitrobenzene has been applied, together with an indication of the type of oils produced therefrom. The amount of solvent used is given for three-stage counter-current treatment, and is based on the charge. The inspections of the product were taken after a normal finishing treatment which included acid treating, clay percolation, and de-waxing. The yields apply to the unfinished "nitraffin."

By reason of its high specific gravity, nitrobenzene operates readily on crude residua of very high viscosity and/or asphalt content. Most stocks in Tables 2 to 5 of viscosity over 200 sec. at 210°F. are crude residua. In this respect nitrobenzene enjoys an advantage over solvents such as phenol, whose relatively low specific gravity renders separation of the phases difficult, if not impossible, with residual stocks.

Table 2 indicates the wide viscosity range permissible in the charging stocks. In all cases a product closely approximating a Pennsylvania oil was produced.

A highly paraffinic oil may be produced from the entire range of crudes. This is shown in Table 3. It will be seen that while the "nitraffin" yield is small for the naphthenic stocks, the volume of nitrobenzene required for the extraction remains within the general range of 100 to 150 per cent.

TABLE 4
Variation in Nitrobenzene-Oil Ratio

Nitrobenzene Per Cent	Charge V.G.C.	"Nitraffin" Yield Per Cent	Finished Oil V.G.C.
150	0.889	24	0.817
200		21	0.801
53	0.853	55	0.817
100		49	0.811
136		44	0.807
185		38	0.804
375		28	0.799
50	0.808	80	0.800
100		47	0.792
350		28	0.779

TABLE 5
Viscosity Differences of Charge and "Nitraffin"

Charge			Finished Oil			
Saybolt Viscosity			Saybolt Viscosity			
At 100 Deg. F.	At 210 Deg. F.	V.G.C.	At 100 Deg. F.	At 210 Deg. F.	V.G.C.	"Nitraffin" Yield Per Cent
152	...	0.844	109	...	0.804	30
305	...	0.853	208	...	0.817	55
			200		0.811	49
			185		0.807	44
			172		0.804	38
			165		0.799	28
	94	0.860		80	0.823	49
	136	0.859		93	0.818	54
	275	0.895		105	0.798	21
	382	0.878		120	0.809	36
	557	0.880		279	0.829	43

The paraffinicity of the product is controlled by the ratio of nitrobenzene to oil in the extraction. This effect is shown for three examples in Table 4. The yields fall off rapidly for high nitrobenzene ratios.

The "nitraffin" invariably has a lower viscosity than the charge. Increasing the nitrobenzene-oil ratio to produce extremely paraffinic oils results in still lower viscosities as well as decreased yields. The viscosity changes given in Table 5 include those due to the finishing treatment.

COLOR REMOVAL BY NITROBENZENE

All save the least efficient of selective solvents remove a large portion of the color bodies with the naphthenic constituents; and, in general, the more efficient the separation between paraffins and naphthenes, the more effective the color removal. On this score also, nitrobenzene was found to be the best of those tested.[6]

In its present state of development, however, the nitrobenzene process will not remove all the color. Reductions ranging from 65 per cent to 95 per cent are readily obtained; but beyond a certain point ni-

trobenzene is no longer effective in removing color, even though it is still capable of further increasing the paraffinicity of the oil. In other words, if it may be so expressed: both naphthenic and paraffinic color bodies seem to exist, but the former predominate. Figure 7 presents data on this point, the stocks ranging from relatively light-colored distillates to very dark bottoms. The "true color" units are approximately additive, and the same as used and explained by Weir, Houghton, and Majewski.[7]

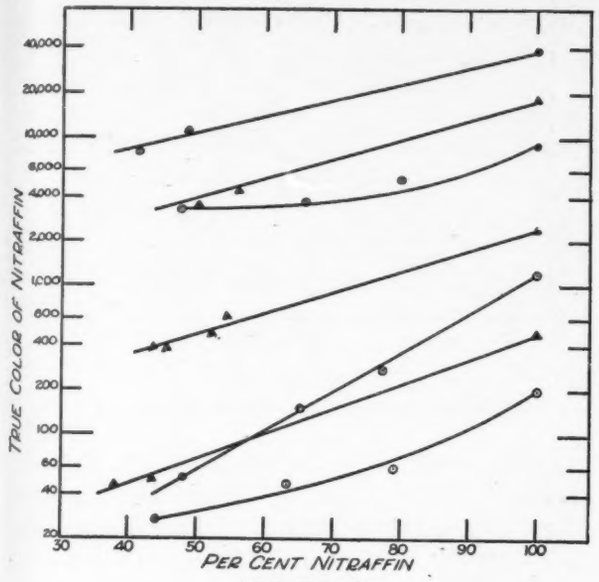


FIGURE 7
Color Removal by Nitrobenzene Extraction.

EFFECT OF WAX ON SEPARATION

Wax is relatively insoluble in nitrobenzene; therefore, most of it is concentrated in the "nitraffin," the pour point of which may be raised as much as 40°F. The "nitraffin" must, therefore, be de-waxed, but behaves normally toward usual methods of de-waxing, such as centrifuging or settling. If the stock is in the paraffin-distillate boiling range, the "nitraffin" may be pressed, but the majority of stocks to which nitrobenzene would be applied are of higher boiling range.

Inasmuch as the wax is usually solid at the temperature of extraction, it has little or no effect upon the efficiency of the solvent; unless it be in such high concentration that it cannot all readily enter the "nitraffin" layer, in which case it may somewhat interfere with clean separation of the "nitrene" layer. In general, stocks up to 100°F. pour point, and occasionally higher, offer no difficulty in handling.

Waxy stocks may, if desired, be de-waxed—totally or partially—before being extracted. In fact, this procedure may be in some cases advisable, even though the presence of the wax would cause no difficulty in the extraction; for the amount of wax to be removed is substantially the same whether it be from stock or "nitraffin," and in the first case the oil remaining on the wax represents stock (low value) which in the second it is "nitraffin" (high value).

CONTAMINATION OF SOLVENT

Nitrobenzene offers little difficulty in the matter of contamination. The solubility of water, for example, is so low that no differences were found in extraction carried out on the same stock with: 1, specially dried solvent; 2, water-saturated solvent; and 3, an excess of water, equal to 25 per cent of the volume of solvent, present during the entire run.

One precaution must, however, be observed: that the stocks contain no light ends boiling within the range of nitrobenzene itself; for such material could obviously not be separated by distillation. Proper fractionation of lubricating stocks obviates this difficulty; but, if such contamination should occur, the solvent may be recovered by crystallization, inasmuch as nitrobenzene forms very large, easily separable crystals at about 41°F.

ECONOMIES IN FINISHING "NITRAFFINS" AND SUPERIOR QUALITIES OF FINISHED OILS

With so much color removed by the nitrobenzene extraction, ecomomies are realized in the finishing treatment. Comparative treatments were made by extracting the stock with nitrobenzene, reducing the "nitraffin" to about the viscosity of the stock, and then finishing both stock and reduced "nitraffin" by identical methods. In general, it was found that by using about 50 per cent as much acid, and taking clay yields as high as, or higher than, those with the stock, the "nitraffins" produced oils superior not only with respect to viscosity-temperature slope, but also flash point and carbon residue. In fact, the carbon residue is reduced to a negligible amount in the distillate products. These inspections are summarized in Table 6.

TABLE 6
Improvement in Quality of Oil

	Viscosity At 210 Deg. F.	V.G.C.	V.I.	Flash Point Deg. F.	Carbon Residue
Mid Continent					
Distillate	69	0.852	83	475	0.46
Distillate "nitraffin".	67	0.811	102	490	0.11
Coastal					
Distillate	84	0.850	47	455	0.53
Distillate "nitraffin".	85	0.803	89	520	0.07
Coastal					
Residuum 159		0.863	..	500	1.0
Residue "nitraffin"...151		0.830	..	535	0.5

A more complete picture of a single treatment is given in Table 7. In this case the heavy distillate from a mixed-base crude was processed to a heavy motor oil of Pennsylvania quality.

PRODUCTION OF OILS OF UNUSUAL PROPERTIES

Heretofore refining processes have in the main been confined to separating lubricating stocks by boiling range, and then removing "impurities" by means of destructive reagents. The range of properties thus obtainable from a given stock is naturally limited; but a method which separates a stock—without chemical change—into any desired number of fractions, each of which is of different composition

TABLE 7
Production of High-Grade Motor Oil

Treatment
Extraction—140 per cent nitrobenzene
Temperature—First stage, 50°F.
Third stage, 77°F.
Yield—52.0 per cent "nitraffin," 48.0 per cent "nitrene."
Acid treatment—62 lb. 66 deg. Baume acid per 50-gal. bbl.
Solution percolation (30-70 mix)—82 bbl. per ton No. 1 Attapulgus clay
Centrifuge de-waxed
No straight percolation

Inspections	Charge	"Nitraffin"	"Nitrene"	Motor Oil
Gravity, deg. A.P.I.....	20.2	26.6	14.6	27.1
Saybolt viscosity at 100 deg. F., seconds	...	...	...	1,038
Saybolt viscosity at 210 deg. F., seconds	136	95	245	94
Viscosity-gravity constant	0.859	0.816	0.897	0.813
Viscosity index				101
"Parvis" temperature, deg. F.				2
True color	2320	474	4500	4
N.P.A. color				1¾
Pour point, deg. F.....	60	100		35
Flash point, deg. F.....	495	500		505
Fire point, deg. F.....	595	585		590
Conradson carbon, per cent				0 01
Ash, per cent				0.002

than the stock, offers much greater possibilities in the production of special oils. Two types of special oils will serve to illustrate this point.

1. Electrical Insulating Oils

An oil may be considered an excellent insulating oil if after subjection to the G.E. oxidation test (exposure to air at 100°C. for 72 hours) it exhibits an electrical resistivity half as great as its original resistivity. Table 8 gives the characteristics of successive fractions made from a single stock. Multiple extraction was employed to produce the various "nitrene" fractions. The first "nitrene" exhibits extremely poor resistivity stability, but each succeeding fraction is progressively better, with the "nitraffin" actually exhibiting an improvement in this particular property when subjected to the test designed to break it down.

TABLE 8
Insulating Oils

Oil Fraction Per Cent of Charge	"Nitrene" 0-19	"Nitrene" 19-47	"Nitrene" 47-69	"Nitraffin" 0-31
Gravity, deg. A.P.I.....	19.5	21.0	26.2	32.2
Saybolt viscosity at 210°F.	457	368	255	176
Viscosity-gravity constant	0.889	0.880	0.843	0.804
Resistivity at 85°C. Initial	4.0	10.6	30.8	5.52
After 72 hours at 100°C.	0.063	0.27	7.0	28.3

While with any stock results of this kind are reproducible, it is not always the "nitraffin" which gives this rather surprising performance. Indeed, it is more frequently an intermediate "nitrene" fraction; never, to our knowledge, a first (i.e., most naphthenic) "nitrene."

2. Special Refrigerator Oil

Oils which are to be used in direct contact with sulfur dioxide as a refrigerant are required to dissolve a minimum of the sulfur dioxide. In one case a maximum of 15 per cent absorbed by the oil in contact with liquid sulfur dioxide at 60°C. was specified.

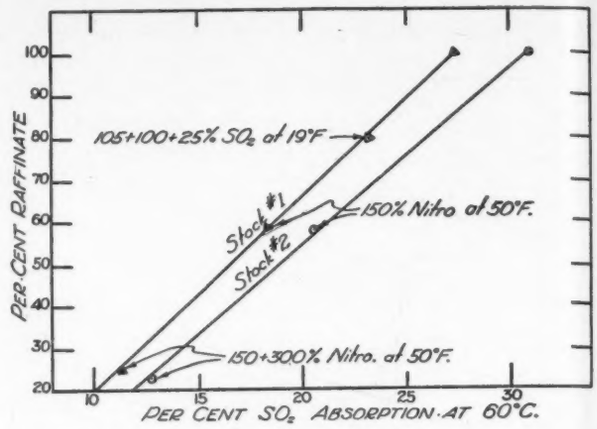


FIGURE 8
Production of Refrigerator Lubricant.

Figure 8 shows how the sulfur dioxide absorption decreases as more of the naphthenic constituents are removed. It is interesting to note that the oil cannot be economically prepared, at least from these stocks, by extraction with liquid sulfur dioxide itself—not because of lack of selectivity, but merely, as pointed out above, because the sulfur dioxide lacks the solvent power to remove a sufficient percentage of the highly absorptive components.

UTILIZATION OF "NITRENES"

It has been frequently emphasized that nitrobenzene extraction brings about no chemical change in the oil; and, therefore, it may be stated that, for purposes other than the manufacture of (paraffinic) lubricating oils, the "nitrene" is as satisfactory as the stock. The economics of the process do not require any greater value for the "nitrene" than that of cracking stock or fuel oil; and, therefore, this phase of the process has received less attention than the "nitraffin" phase. There is every likelihood, however, that the "nitrenes" will prove to be a source of decidedly more valuable products. Naphthenic lubricating oils have their sphere of usefulness, and vacuum distillation of the "nitrenes" readily yields excellent overhead products which are more naphthenic than would have been similar distillates from the original stock.

PLANT HAZARDS

Hazards in handling nitrobenzene are not nearly so serious as first thought might suggest. It is not highly flammable, having an open-cut flash of about 210°F. It is unquestionably toxic, but in the long history of nitrobenzene manufacture fatalities have been very rare. Poisoning may occur either: 1, by contact of the liquid with any portion of the skin; or, 2, by inhalation of the vapors. The first mode is by far the more dangerous, but is substantially eliminated if the men are cautioned to wash the nitro-

benzene off immediately, or to remove any wearing apparel which is saturated with nitrobenzene. The dangers of vapor poisoning are minimized; because: 1, its odor is marked and easily recognizable; 2, long exposure is required for serious effects; and, 3, symptoms are readily detected either by the victim himself or those near him, and usually appear early enough that proper treatment may be applied.

In our own experience, covering almost five years of laboratory and semi-plant development, we have encountered no difficulty; although we have, of course, adopted all reasonable precautions. There are very good reasons, however, why poison hazards will be almost non-existent in a nitrobenzene plant, for such hazards can be set up only when the solvent escapes from within the plant. As will be fully discussed later, economic considerations make it imperative to adopt definite precautions to the end that no nitrobenzene shall escape; and these same measures are the most effective safety provisions which could be established.

Finally, nitrobenzene and oil react violently at temperatures above 450°F.; but, as will be developed, there is no necessity for such temperatures. Indeed, in the plant as designed there is no possibility of reaching them.

RECOVERY OF SOLVENT

It is apparent that profitable operation of a nitrobenzene plant is directly dependent upon the ability to reduce solvent losses to a minimum. Preliminary calculations were based upon a loss of 0.2 per cent by volume of the nitrobenzene used, per cycle. Even at this low figure this item represented nearly 40 per cent of the entire extraction cost, and many and persistent were the apprehensions upon the matter of expense due to solvent loss—for nitrobenzene is an oxidizing agent—and there was every reason to suspect that the unrefined stocks with which it would be in contact contained oxidizable material. No small amount of the investigational work, therefore, was devoted to the task of dispelling this anxiety from the minds of all concerned.

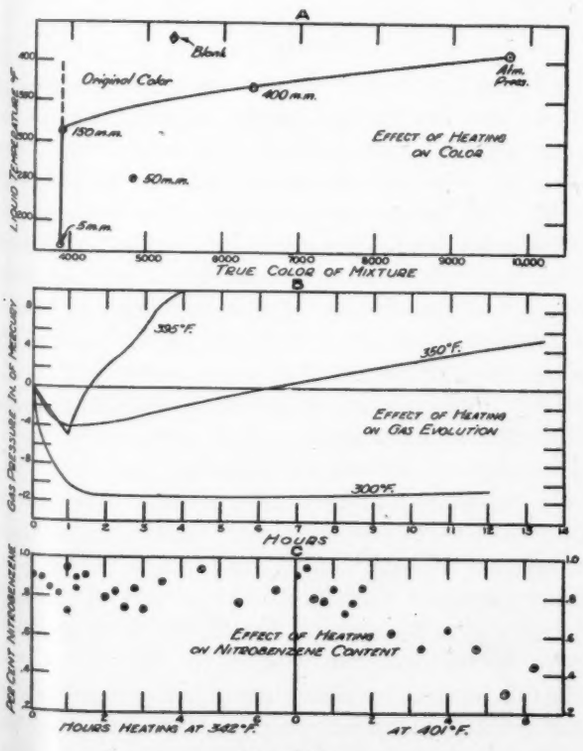


FIGURE 9
Stability of Nitrobenzene in Oil Mixtures

One test, or many tests by any one method, did not, however, suffice. Recourse was had to four different attacks, which will be briefly described. In each instance the stocks used were asphaltic crude residua, selected as being most apt to contain unstable compounds.

1. On both laboratory and semi-plant scale, the nitrobenzene used in an extraction was recovered by distillation, and either measured or weighed. Substantially complete recovery was indicated.
2. Any marked reaction between oil and nitrobenzene results in a heavy tar of extremely dark color. A 50-50 mixture of oil and nitrobenzene was, therefore, refluxed at various temperatures (controlled by pressure) for one hour, and the color of the mixture determined. No reaction was indicated (Figure 9 A) below about 350°F. (note position of blank containing lamp oil distillate instead of nitrobenzene), although reaction was positive at 367°F. and at 412°F.
3. Reaction between oil and nitrobenzene is also accompanied by copious gas formation. A 65 per cent nitrobenzene—35 per cent oil mixture (corresponding roughly to a "nitrene" layer) was, therefore, sealed into glass tubes, and heated to definite temperatures (in the presence of air) for long periods, noting the pressure at intervals. In each instance air was dissolved during the heating period, but thereafter (Figure 9 B) the tube at 300°F. showed no gas evolution, at 350°F. slight, and at 395°F. marked evolution. The gas was analyzed and the nitrobenzene recovered by distillation. The physical properties of the nitrobenzene recovered were unchanged from the original. Calculations showed a reaction loss of approximately 0.06 per cent of the nitrobenzene per period of 15 minutes, which is probably greater than the actual distillation time for any one portion of material.
4. As will be indicated in the discussion of the plant, most of the nitrobenzene is removed at temperatures scarcely above 200°F., but the removal of the last portions requires higher temperatures. Therefore, about 1 per cent of nitrobenzene was added to oil; the mixture

(Continued on page 581)

Corrosion in Non-Pressure Refining Equipment

S. S. SHAFFER and J. E. POLLOCK
Humble Oil & Refining Company, Houston, Texas

This paper was read before Thirteenth Annual Meeting American Petroleum Institute, at Houston, November 15, 1932.

THE general subject of the corrosion of non-pressure refining equipment covers so large a field that it would be impossible for all phases to be handled adequately in a single paper for presentation at this meeting. It has, therefore, been decided to confine the discussion largely to one phase of the subject, viz., the protection of condensing coils by the use of ammonia—this extended discussion being accompanied by a brief resume of plant experience with other refinery corrosion problems. To this end the subject matter will be treated under the following main equipment headings: 1, tanks; 2, lines; 3, stills and fractionating equipment; and 4, condensers.

The oil flow in the refinery is well known, but for the sake of agreement on nomenclature it will be briefly outlined. The crude oil is received from the pipe line company into crude oil storage tanks of 55,000- to 93,000-barrel capacity, from which it is pumped through charge lines to batteries of shell stills or pipe stills equipped with fractionating towers—the crude charge being in heat exchange with the still vapors, thus providing some fractionating reflux as well as heat economy. The oil passes in series flow, steam being used as an aid to distillation—in those stills taking off the heavier cuts—until the bottoms are withdrawn as fuel or to be further reduced in vacuum towers. Cuts are segregated or combined according to stocks required. Distillation from atmospheric pipe stills is in effect very similar; time of contact in the furnace is shorter, but steam may be used or not in the tower as desired. From the fractionating towers the vapors pass by means of large-diameter vapor lines to the condensers, either of the closed tubular or open-box coil type, from which the condensed oil passes by run-down lines through a receiving house—where the flow can be observed—to a run-down tank (1200- to 2500-barrel capacity). Should it be necessary to obtain efficient fractionation, a portion of the condensate, taken directly from the stream or from a small tank which serves as an accumulator or water separator, is pumped back to the fractionating tower as wash—the lines from the accumulator to the tower being known as wash lines. From the run-down tanks the various fractions are pumped to intermediate storage tanks, varying in size from 10,000- to 80,000-barrel capacity, according to future disposition of the oil. Gasoline and kerosene cuts requiring doctor sweetening are then pumped through sweetening units and thence to finished storage, where they are available for blending purposes. Other cuts comprising furnace oil, gas oil or cracking stocks are shipped, or charged to cracking units. Cracked distillate when debutanized is stored under atmospheric pressure in 14,000- and 17,000-barrel tanks, from which it is pumped to acid treaters and, after caustic neutralizing, returned to storage for accumulation for re-running; the re-run distillate is then handled similarly to straight-run distillate—being collected in storage, doctor-sweetened, and then placed in finished storage as a blending stock.

The corrosiveness of the oil will thus vary from one piece of equipment to another according to previous treatment. The factors influencing corrosion will be considered as the equipment is dealt with.

TANKS

Steel tanks in finished gasoline service require no attention from the corrosion point of view, the service being sufficiently long that protection is unwarranted. In the case of crude, run-down, and intermediate services the roof suffers most severely, the bottom next, and the sides least. The corrosion of the roof is due to hydrogen sulfide, moisture, and air. Roofs on crude tankage will usually last from four years upward; on run-down tanks, an average of about six to seven years —some being as low as 3½ years and as high as 10 years—on intermediate storage for cracking stocks and gas oils, 2½ to six years or more.

An enormous amount of work has been done, both by the oil industry and by paint manufacturers, in attempts to develop suitable paints for the protection of the interiors of steel tanks. A recent publication[1] lists the characteristics necessary if the paint is to withstand the extremely corrosive conditions which exist in this service. Certain coatings have given fairly satisfactory protection, and experience shows that as much as two years' protection can be expected from the best types; but even if this service is obtained, calculation of the cost of application will usually show it can only be justi-

fied where corrosion is so severe that the unprotected roof would last for only three years or less. It has not been found economical to paint the interior of tank roofs after they have been corroded in service. This is largely on account of the cost of the very thorough cleaning required (including sand blasting) and the infeasibility in most refineries of taking tankage out of service for a period long enough to complete the cleaning and painting job.

On run-down tanks aluminum roofs have been tried with some success. One is over four years old, and has required no attention; and a number have been in service for 18 months without any evidence of corrosion other than the presence of a small amount of white powder (aluminum oxide) resulting from hydrolysis of aluminum sulfide.

Roofs of galvanized iron have also been tried in paraffin cracking-stock service; these also show no signs of corrosion after 20 months, other than the formation of a light white powdery deposit.

In some cases, where replacements of steel in crude and intermediate services have been necessary, these have been made by changing the construction to floating roofs, thus eliminating the vapor space. Corrosion —this time atmospheric—is transferred to the inside of the shell; in the case of the light oils where oil drainage when the tank is pumped is rapid, the sides rapidly form scale, although the condition is not quite so bad as it looks. When such a tank is cleaned, the accumulation of scale around the inside edge of the tank looks considerable, but it must be remembered that it has come from a surface 35 feet to 40 feet high. After 18 months loss of metal could not be detected in test holes by means of calipers. The underside of the floating roof in the same period showed very little effect generally; although manholes where gas can collect can be expected to suffer corrosion, but not to the same extent as cone roofs, as the supply of oxygen is limited in such places.

In those cases where caustic washing is a regular part of the treatment of a stock, intermediate tankage can be protected by arranging the caustic wash before storage; in this way hydrogen sulfide is removed, thus reducing corrosion of tankage considerably. In the case of pressure distillate, debutanization removes hydrogen sulfide from the stock, the completeness depending on the extent to which volatility is reduced; this also serves to reduce tankage corrosion.

Tank sides, other than the top ring, rarely suffer corrosion comparable with the roof, and no protection is given, although it has been proposed to try a thin cement layer.

The tank bottoms suffer from the water (and the impurities it contains) that usually accompanies the oil; in the case of crude oil, salt water containing hydrogen sulfide; in distillates, hydrochloric acid as well as hydrogen sulfide; and in re-run distillates from acid-treated stocks, sulfur dioxide. Concrete and other coatings have been used successfully in saving the replacement of bottoms that have corroded through in places. When caustic washing of an oil is employed, there is frequently enough carry-over of caustic to reduce the action which would otherwise take place.

Turning to wash drums, separators, and water settlers: the corrosion is of a nature similar to that suffered by tank bottoms, but much more severe. In these cases it is usually the bottoms, sides, and baffles which corrode most rapidly. Water and the impurities present are responsible; from crude distillation the lighter streams invariably contain hydrochloric acid as well as hydrogen sulfide; the heavier streams contain water from steam used in distillation, and hydrogen sulfide; and all streams where steam is used contain carbon dioxide from the steam, unless precautions have been taken to exclude it at the boiler house. It will be recognized at once that corrosion will be worse in equipment handling the lighter streams. In certain severe spots it becomes necessary to use special corrosion-resistant metals, such as 18-8 chrome-nickel steels and alloy cast-irons, for drains and draw-off lines; lines to separators should enter well into the drum to avoid acid water running down the inside of the shell. The bottoms of such drums are frequently lined with concrete.

LINES

In the consideration of lines it will be recognized that they are subject to all the influences that affect tankage, except that possibly less air is present. However, as the lines are usually underground, external corrosion enters as an additional factor to be considered. In the case of crude charge lines in the Gulf Coast district, external corrosion is more severe than internal; thus, steel lines are satisfactory if they are protected externally. In the sour distillate services steel is rapidly corroded; and external protection would be wasted money. The larger steel lines, eight-inch, 10-inch, and 12-inch, have been pitted through externally in 10 years, and the smaller lines in less time; when the penetration from the inside is less than this, steel is used with external protection, and when it is greater, cast-iron, unprotected externally, is used. Thus, in general steel is used for crude charge, pressure distillate, caustic, washed fractions, fuel bottoms, and finished oil; cast-iron has been found more suitable for unwashed naphthas, kerosenes, and re-run distillates. Special alloys, such as 18-8 chrome-nickel steels and alloy cast-irons, are used as indicated under the paragraph on wash drums and separators, the 18-8 alloy usually being discarded high-pressure tubing.

Gas lines also in some cases suffer very rapid deterioration, especially when wet gas is transferred. Still gases, after removing gasoline by compression, are very corrosive; a 12-inch steel line in such service lasted two years; the gas contained a high percentage of hydrogen sulfide and air, and the scale formed on the inside was sufficient to cause a pressure drop that affected operation materially. Replacement was carried out in two sections, zinc and lead coated respectively, to determine if such means of protection are satisfac-

tory. To date the line is still in service after 14 months, no inspection having been made.

STILLS AND FRACTIONATING EQUIPMENT

In crude stills of the shell type corrosion has been found to be surprisingly small; in the vapor space this is almost negligible, while in the liquid space it is usually of less account than the destruction from the furnace side. Excessive firing results in a brittle scale forming on the furnace side of the shell; return tubes usually suffer from the same cause for a short distance from the back of the still. This comparative freedom from corrosion is in all probability due to the "dryness" of the oil or vapor, since vapor lines and fractionating towers also cause very little trouble, with the exception of plate drain seal over-flows; even when steam is used, the temperature is such that it does not condense except in very localized places. When wash is pumped back to the tower and water is incompletely separated, the top plate at least is likely to suffer. Cast-iron plates and caps in a steel tower have proved very satisfactory in service.

Very localized corrosion frequently occurs in crude preheaters where vapor from the bubble towers is exchanged against the incoming crude charge. Sludge and water (including salts) from the crude may accumulate as a slop and attack the outside of the tubes through which the vapor is passing. When this occurs, the condition is very hard to rectify.

Following the vapor overhead from the bubble tower, corrosion begins as soon as condensation begins, as water condenses and dissolves the accompanying acid, hydrochloric and hydrogen sulfide in the case of crude distillation, and sulfur dioxide (sulfurous acid) in the case of re-run operations.

This brings corrosion of condensers and their protection into consideration.

CONDENSERS

A large proportion of the condensers in use consist of the coil-type, steel or cast-iron pipe immersed in water in an open box. More recent practice tends toward the use of closed-type shell and tube condensers for distillation equipment, the open-box type still being favored for cracking installations.

Corrosion of coil-type condensers and experimental work in combatting it by means of ammonia have been dealt with previously.[2] The life of these condensers was indicated for various services; 4.5 years for light streams (naphtha), 10 years or more for heavy distillates (kerosene and heavier) from crudes, 4.7 years for light naphtha from re-distillation of acid-treated stocks, and six years or more for heavy naphtha from untreated cracked stocks. (A revision of these figures will probably show slightly lower service for light naphtha from acid-treated stocks.) Reduction in iron loss off rom 75 per cent to 95 per cent by the experimental injection of ammonia into the vapor line immediately before the condenser was also indicated. It is, of course, recognized that other alkalies, such as caustic soda and milk of lime, may be used as neutralizers whenever cheapness or convenience indicates. The application of ammonia on a plant scale to the reduction of condenser corrosion will now be considered in some detail.

AMMONIA UNIT

Equipment for an ammonia storage and distributing system is relatively simple. A drum or two drums (discarded pressure drums from cracking equipment are usually satisfactory), capable of withstanding 200 pounds per square inch pressure and having a capacity of 50,000 to 60,000 pounds of liquid ammonia in order to unload a tank car of 50,000 pounds, will provide enough storage for almost any ordinary purpose. A light roof to cut off the direct rays of the sun is all that is necessary as a covering for the storage drums, provision for supplying heat (such as a small steam coil) being desirable during the colder months. Distribution of ammonia gas is made by one-inch steel lines reduced to one quarter-inch at each condenser; control of each stream is effected by a needle valve in a commercial meter of the manometer-type, which also indicates the rate of flow in cubic feet per minute. Total amounts to each unit may be measured separately by recording meters on each main line or by passing all the gas through one meter and prorating the amount back to each unit by the meter settings. The liquid ammonia pressure is reduced by two valves, to 110 and 45 pounds, respectively, so that the gas is easily delivered to the condenser vapor line against the usual 0 to two pounds per square inch back pressure. Connection to the vapor line is made by an inverted U-bend to prevent condensate collecting and running into the meter. Arrangements are also made to feed a small quantity of water to the vapor line, so that the normal amount present may be augmented if necessary to ensure removal of ammonia salts. (See Figure 1.)

REQUIREMENTS OF VARIOUS CRUDES

Not all streams from the same crude nor all crudes require the same treatment. As hydrochloric acid is the main cause of corrosion of condensers on crude batteries, the most serious effect will be expected towards the front end of the battery, and the intensity of the corrosion will depend largely on the amount of water present in the crude and the salinity (calcium and magnesium) of the water. The point of greatest intensity of corrosion will depend largely on the treatment of the crude. High distillation temperatures and the hydrolytic effect of steam favor the breakdown of calcium and magnesium chlorides, so that for light crudes of low salinity very little corrosion may be caused by the first two or three streams; but, as the distillation temperature is raised and steam is used, more hydrochloric acid is evolved; even in some of these cases, however, the amount is small and, as such, can be neglected. Northeast Texas crude will be shown to be one of this type. On the other hand, a crude like Salt Flat,

fairly deficient in light ends and requiring the use of steam in the first still, represents serious corrosion difficulties in the first two condensers—the remainder

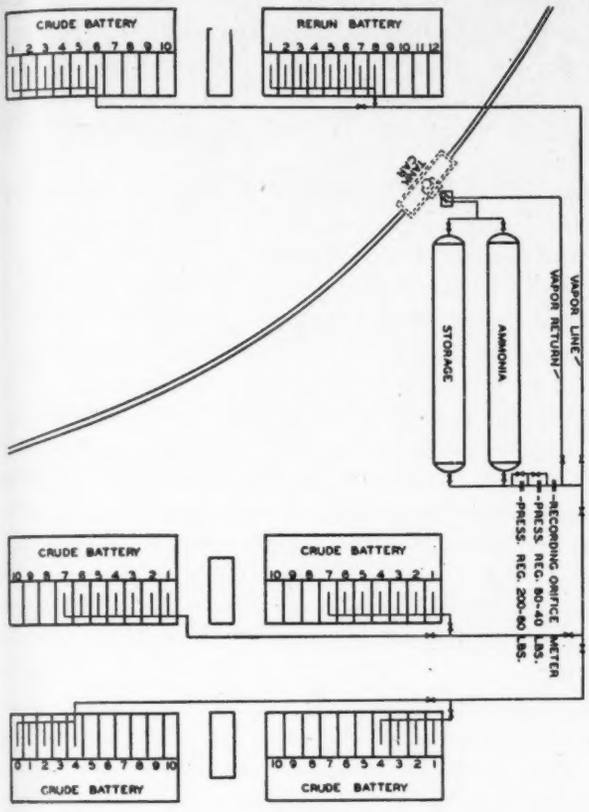


FIGURE 1

being comparatively free from corrosion, since the calcium and magnesium chlorides have almost completely broken down. Some variation will be shown from day to day even with the same crude, due to variations in operating conditions and in the calcium and magnesium chloride content of the crude.

Another factor that will be subject to still conditions is the hydrogen sulfide content of the streams, which may have some effect on corrosion; but it will be seen later that a relation exists between the hydrochloric acid produced (or chloride present) and the iron losses, that appears singularly independent of at least moderate amounts of hydrogen sulfide.

The question to be considered is how to measure the extent of the corrosion and the regulatory control measures to be adopted in combating it.

CONTROL MEASURES

The purpose of the addition of ammonia is primarily to neutralize the hydrochloric acid condensed in the distillate. An obvious method of control would be determining the *pH* value of the separated water and so adjusting the ammonia until neutrality is reached. Colorimetric determinations are not always easy, owing to the color of the water, which frequently contains iron sulfide in suspension or solution; electrical determinations would involve additional labor and expense; too close and too frequent control seems unnecessary. A second method which has been practised is actually to determine the amount of chloride and iron present in each stream. A number of determinations have shown that the iron-chloride ratio is approximately 0.834 in such cases as when no ammonia is used; this on an equivalent basis approximates 1.06:1. Thus, if ammonia is added in slight excess of the amount equivalent to the chloride, the iron loss will be taken care of.

From a large number of *pH* determinations, iron losses from streams are seen to become small in the range *pH* 5 to 7, even though the amount of water present varies considerably; therefore, it can be concluded that it is not necessary to neutralize completely to *pH* 7. This, in other words, means that to move the *pH* value from 5 to 7 involves neutralizing the hydrogen sulfide which is almost always present, but which in a closed condenser is harmless (in the absence of air) compared with hydrochloric acid.

Typical results are given for various crudes.

NORTHEAST TEXAS

Table 1 illustrates the results from a mixed Northeast Texas crude; a small amount of ammonia was being delivered to the second coil, but this was subsequently discontinued—the iron loss on all the condensers being considered low. The iron to chloride ratio of 0.92 was higher than the average value of 0.834 mentioned above.

SALT FLAT CRUDE

Results during the addition of ammonia to Salt Flat streams are given in Table 2. The ammonia being used was regulated as follows:

Still No.	0	1	2	3	4
Ammonia, cu. ft. per min.....	0.3	0.2	0.15	0.15	0.10

The iron loss amounted to six pounds per day, or a reduction of 87.5 per cent on the basis of the chloride present—60.19 pounds being equivalent to 48 pounds of iron without the use of ammonia. Even so, the results indicate the possibility of reducing the amount of ammonia without materially impairing the results.

REAGAN CRUDE

Table 3 gives the results for Reagan crude; at the time of the test the rates of delivery of ammonia to the various condensers were as follows:

Still No.	1	2	3	4	5	6
Ammonia, cu. ft. per min....	0.10	0.15	0.15	0.10	0.10	0.10
These rates were subsequently reduced as follows:						
Ammonia, cu. ft. per min....	0.10	0.10	0.10	0.05	0.05	0.05

Ammonia was eventually cut out from the sixth still altogether.

PANHANDLE

The set of results in Table 4, illustrating the effect of Panhandle crude, shows the third still to be producing the greatest amount of acid; however, even though the amount of ammonia used in the corresponding condenser is only 54 per cent of the theoretical requirement, a reduction of over 80 per cent of the iron loss has been effected.

From these results it will be seen that it is possible to reduce iron losses by 80 per cent to 90 per cent in the condensers by means of approximately three pounds

TABLE 1
Northeast Texas Crude—19,400 Barrels Per Day

Still No.	Pounds Per Thousand Barrels of Crude: Chloride Cl′	Iron Loss	Ammonia Used	Per Cent Excess Ammonia Used	Pounds Per Day: Chloride Cl′	Iron Loss	Ammonia Used	Equivalent Relation Fe″ to Cl′
0′	0.052	0.035	None	None	1.0	0.66	None	0.845
0*	0.022	None	0.165	1,500	0.42	None	3.2	....
11*	0.108	0.124	None	None	2.1	2.4	None	1.46
12*	0.22	0.212	None	None	4.25	4.1	None	1.22
13*	0.266	0.223	None	None	5.15	4.33	None	1.07
14*	0.022	0.021	None	None	0.42	0.4	None	1.21
Total	0.69	0.615	0.165		13.34	11.9	3.2	1.16
				Iron-chloride ratio:	0.92			

*Steam

TABLE 2
Salt Flat Crude—15,700 Barrels Per Day

Still No.	Pounds Per Thousand Barrels of Crude: Chloride Cl′	Iron Loss	Ammonia Used	Pounds Per Day: Chloride Cl′	Iron Loss	Ammonia Used	Per Cent Excess Ammonia Used	Ammonia Required, Assuming Complete Neutralization of Acid (Cl′): Pounds Per Day	Cubic Feet Per Minute
0	1.43	0.056	1.23	22.5	0.87	19.3	79	10.75	0.167
1*	1.46	0.071	0.82	23.0	1.11	12.9	17	11.0	0.17
2*	0.37	0.096	0.62	5.8	1.50	9.66	246	2.80	0.044
3*	0.39	0.089	0.41	6.13	1.39	6.44	118	2.95	0.046
4*	0.176	0.0726	0.41	2.76	1.14	6.44	386	1.32	0.021
Total	3.826	0.384	3.49	60.19	6.0	54.74	90	28.82	0.447

*Steam

TABLE 3
Reagan Crude—13,700 Barrels Per Day

Still No.	Pounds Per Thousand Barrels of Crude: Chloride Cl′	Iron Loss	Ammonia Used	Pounds Per Day: Chloride Cl′	Iron Loss	Ammonia Used	Per Cent Excess Ammonia Used	Ammonia Required, Assuming Complete Neutralization of Acid (Cl′): Pounds Per Day	Cubic Feet Per Minute
1	0.14	Trace	0.47	1.93	Trace	6.44	590	0.93	0.015
2	1.29	Trace	0.70	17.70	Trace	9.66	14	8.50	0.132
3	0.057	Trace	0.70	0.79	Trace	9.66	2,440	0.38	Negligible
4*	0.27	Trace	0.47	3.69	Trace	6.44	263	1.77	0.028
5*	0.21	Trace	0.47	2.90	Trace	6.44	360	1.40	0.022
6*	0.378	Trace	0.47	5.19	Trace	6.44	157	2.50	0.04
Total	2.35	Trace	3.28	32.20	Trace	45.08	192	15.48	0.114

*Steam

TABLE 4
Panhandle Crude—12,600 Barrels Per Day

Still No.	Pounds Per Thousand Barrels of Crude: Chloride Cl′	Iron Loss	Ammonia Used	Per Cent Excess Ammonia Used	Pounds Per Day: Chloride Cl′	Iron Loss	Ammonia Used	Ammonia Required, Assuming Complete Neutralization of Acid (Cl′): Pounds Per Day	Cubic Feet Per Minute
1	0.23	0.016	0.26	136	2.9	0.2	3.2	1.34	0.021
2	0.11	0.011	0.77	1,370	1.4	0.14	9.7	0.65	Negligible
3	1.97	0.29	0.51	—46	24.9	3.7	6.4	11.9	0.185
4	0.22	0.113	0.26	144	2.8	1.4	3.2	1.33	0.021
Total	2.53	0.43	1.80		32.0	5.44	22.5	15.22	0.238

No steam.

of ammonia per 1000 barrels of crude. When a rate has been set for each condenser, an occasional check-up will indicate whether this appears to be distributed to the best advantage. Conditions in each still will not always be the same, so that at different times different units will be subject to the greatest corrosive action; it is deemed inadvisable, however, to attempt to follow this shift too closely, as the greatest effect is taken care of. It is very difficult to assign any limit to the permissible loss, but at present the use of three pounds per 1000 barrels in reducing the loss 80 per cent to 90 per cent brings it well within five pounds of iron per day per condenser, so that such a figure has been tentatively adopted as a deciding limit whether ammonia should be used; and, if used, as the measure of its sufficiency.

The effect in the case of re-running acid-treated stocks is very similar, except that sulfurous acid is the corrosive agent in place of the hydrochloric. The sulfur dioxide evolved is the result of the break-down of sulfonic esters formed in treating, and the amount of these present appears to be dependent on the intensity or extent to which cracking is carried out and, therefore, on the amount of unsaturates and aromatics and on the amount of sulfuric acid used in treating; time and conditions of distillation also affect the break-down of these esters considerably; long time, high temperature, and steam increase decomposition.

So far the type of condenser under consideration has been the coil-type immersed in water in an open box. When uncertainty of water supply is not important and economy of space is necessary, the more efficient closed-type exchangers are usually installed. Two such installations using admiralty tubes are in use on the first still each of two batteries, and the service obtained has varied considerably. In one case, where lighter crudes are run and steam is not required in the still, the service obtained has been 2½ years or longer; whereas in the other handling heavier crudes, involving the use of steam, the life has been as low as eight months. Failure has been due to both leakage and to such an accumulation of scale that operation of the still was impossible because of pressure drop through the condensers. The scale consists almost entirely of copper sulfide; and, although ammonia has been tried, examination after operation for one month showed that it was not entirely successful in preventing this scale formation. Tests carried out in the water separated from the condensate at this location have indicated that monel metal would offer no greater resistance than admiralty, and a pure (electric) iron even less. Such destructive conditions are not experienced in steam stripping-still condensers where hydrochloric acid is absent and where there is a plentiful supply of hydrogen sulfide. The problem is principally one of combating the effects of hydrochloric acid.

It is not thought or intended that the methods of combating corrosion cited here are exhaustive, but rather the purpose has been to indicate certain measures which have been taken in the hope that they may be the means of stimulating interest with a view to determining the best means to be adopted in particular cases of severe corrosion.

BIBLIOGRAPHY

[1] Brian Mead, Ind. Eng. Chem., 24, 857 (1932.)
[2] S. S. Shaffer and J. E. Pollock, "Metal Losses in Condensers and Combating Corrosion," Oil Gas J., vol. 30, 46, 78, (1932.)

Presented at Thirteenth Annual Meeting, American Petroleum Institute, Houston, Texas, November 15, 1932

Replacing Sections of Rivited Bubble Tower Shell

WALTER SAMANS
Chief Engineer, The Atlantic Refining Company, Philadelphia, Pa.

THIS particular method of major replacement is shown in Figure 1 for two bubble towers which were made up some years ago from shells then in place and formerly used as part of a thermosyphon-circulation cracking process. The corrosion rate on the lower rings of the tower was much greater than anticipated, due to having to run sour crudes.

When the serpentine coil-type of furnace heater was added, many of the original foundations were used; and the available space being limited, the two towers involved were left in their original location, together with the addition of similar old shells which became part of the modified cracking stills. However, at that time these two towers became bubble towers and had

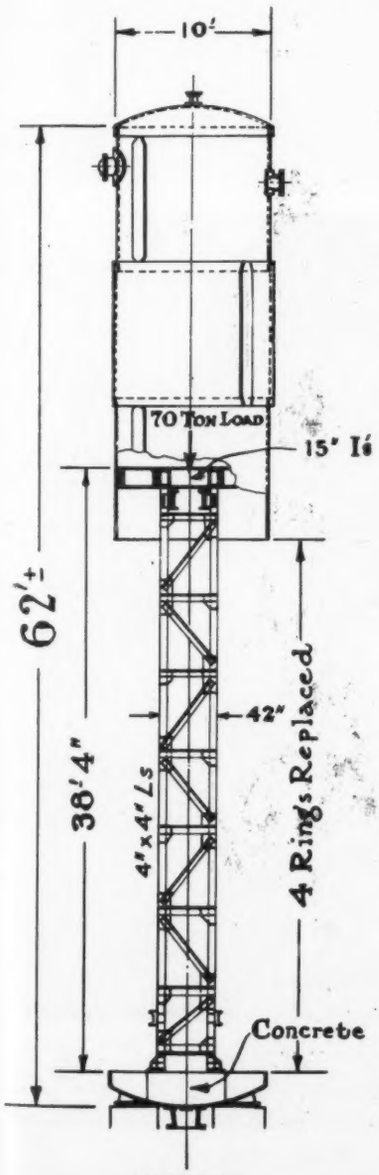


FIGURE 1
Replacing Bubble Tower Sections.

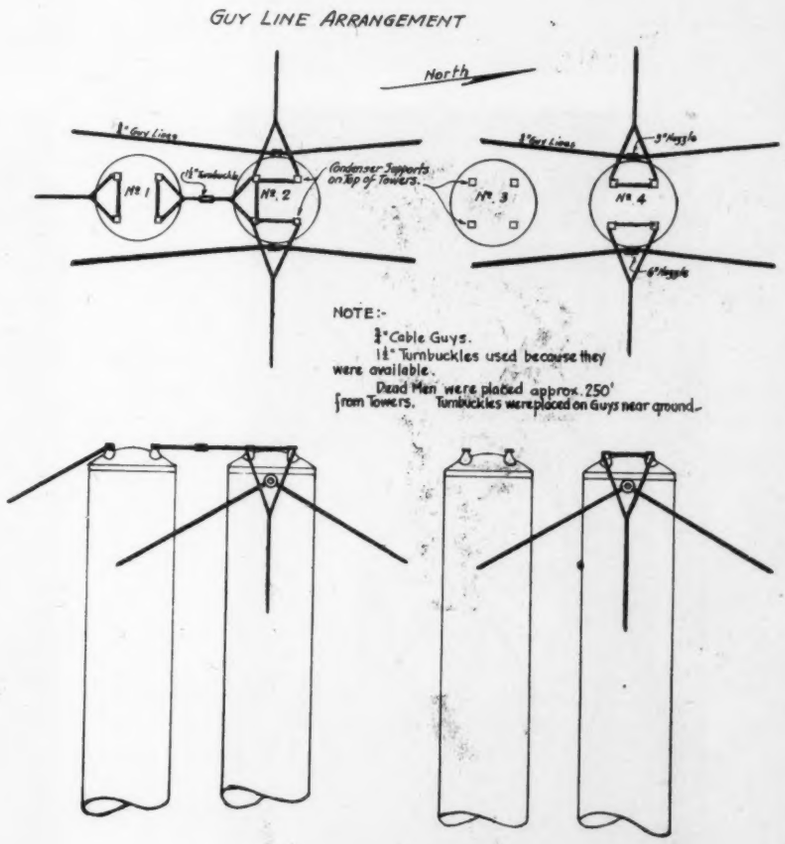

Guy Line Arrangement
North
No. 1
No. 2
No. 3
No. 4
Condenser Supports on Top of Towers.
NOTE:-
¾" Cable Guys.
1¼" Turnbuckles used because they were available.
Dead Men were placed approx. 250' from Towers. Turnbuckles were placed on Guys near ground.

FIGURE 2
Guy Line Arrangements for Towers.

the usual number of trays added in the upper section with a few stripping trays in the lower section.

When it became necessary to replace these two bubble towers on account of excessive corrosion in the lower rings, it was realized that for only two towers in this crowded location the expense of rigging up equipment for replacing them in their entirety would be too great —this cost being estimated at about $49,000.

The upper trays and upper rings and head of the shells and existing piping were perfectly good for many years to come, and it was decided to replace the four lower rings only, including minor interior changes within this limit.

Figure 2 shows the arrangement of guy cables used in setting the top of the tower.

A structural column made up in sections of less than 10 feet was then passed through the lower manhead and erected upon a concrete block especially placed in the tower bottom for this purpose.

The new rings were made up in two sheets per ring, and the original plan was to remove about two thirds of an old ring and place one of the new sheets, temporarily bolted, and then to cut away the balance of the old shell for that ring to place the second sheet. It was found that this was not necessary.

In actual operation it was found that the tower was quite steady; and, while originally the plan was modified to cut out most of the old ring except two ligaments as shown in Figure 3, it actually was found possible on the second tower to cut away the entire shell for all four rings, as shown in Figure 4, looking upward, and Figure 5, giving a closer view from a higher level.

Figure 6 shows the lower end of the upper three rings that remain, and Figure 7 shows the fourth ring sheet hanging in the falls, ready to place.

Figure 8 shows the fourth ring in place, next to the upper section which still retains the insulating jacket, connected piping, and supporting platform.

The cost for the replacement of rings, including removal of insulation and some of the piping, was $25,000.

The shut-down time was about three weeks for the two towers, including some overtime work.

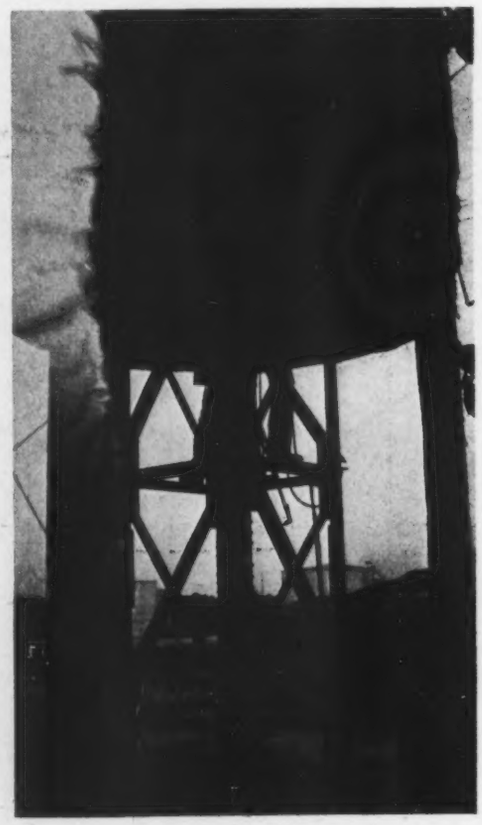


FIGURE 3

View Showing Center Support and Part of Fourth Ring to Be Dismantled.

FIGURE 4

View Looking Northeast and Up, Showing Center Support and part of Fourth Ring to Be Dismantled.

FIGURE 5
View Showing Ligaments of Old Sheets Remaining When Ready to Place New Sheets on Fourth Ring of First Tower.

FIGURE 6
View from Higher Elevation Looking Toward Upper Section of Tower.

FIGURE 7
View of Fourth Ring Sheet Hanging in Falls Ready to Place.

FIGURE 8
View from Furnace Roof, Fourth Ring in Place.

Use of Petroleum Coke As Boiler Plant Fuel

O. F. CAMPBELL
Sinclair Refining Company, East Chicago, Indiana

Paper presented at Thirteenth Annual Meeting American Petroleum Institute, at Houston, November 16, 1932.

DUE to the general plant expansion of the Sinclair Refining Company's plant at Houston, Texas, in 1931 it was necessary to increase the steam generating capacity. Two boilers were installed, each having an average steam output of 120,000 pounds of steam per hour, with a maximum capacity of 148,000 pounds per hour. The boilers are of the Sterling type, and the general layout is shown in Figure 1. Each boiler has 12,250 square feet of heating surface. Each air preheater has 16,964 square feet of heating surface, and is of the tubular type. The superheaters are of the conventional convection type, and each has 2270 square feet of heating surface. With future possibility of electric power generation, the boilers were installed for 600-pound pressure at superheater outlet. At present the boilers are operating at 170 pounds gage and 150° F. of superheat.

When turbo-generators are installed and the boiler pressure increased to 600 pounds, additional superheater surface will be installed to provide a total steam temperature of 750° F. at superheater outlet. The total superheater surface will then be increased to 5130 square feet.

In view of a surplus of petroleum coke breeze for which there is not a ready market, the new boilers were equipped to burn petroleum coke breeze in conjunction with surplus refinery gas and unmerchantable fuel oil. Figure 1 shows the general layout of furnaces, boilers, coke bunkers, pulverizing equipment, etc.

The boiler furnace construction consists of all four walls water-cooled by means of a refractory-covered-block water wall. The furnaces are of the slag-tapping type, and slag is tapped approximately once every two weeks, depending upon the per cent of ash in the coke and the amount of coke consumed. The slag is sluiced by a conventional ash-sluicing system directly to an ash pit, where the slag is removed by a clam-shell bucket crane. The slag pit is so located that the crane can remove the slag from the slag pit when the crane is located on coke-unloading tracks.

The ash content of the coke consists primarily of caustic (NaOH). The caustic content of the coke is caused by coking petroleum residues of high caustic content. Water walls were installed to keep furnace maintenance to a maximum. The water-wall construction consists of cast-iron blocks bolted to the wall tubes. The furnace side of the cast-iron blocks is covered with refractory in order to maintain as high a furnace temperature as possible. The water wall tubes cool the cast iron refractory-covered blocks and prevent the refractory face of the block from fluxing with the caustic content of the coke ash. The caustic content of the coke would readily flux down an ordinary refractory wall. There have been no water-wall repairs or replacements made to date, or over one and one third year's practically continuous service. No water wall movement has been noted to date, and no difficulty has been encountered with furnace bottoms. The furnace bottoms are covered with plastic chrome ore to prevent slag penetration. The chrome ore is heavier than the molten ash which allows the molten ash to float and be tapped off.

The mild climatic conditions at Houston are such that a transite-board steel-supported building was erected in order to reduce capital investment. No building repairs have been made to date, and from all appearances to date no repairs will be required for a long time.

Coke is weighed by means of railroad scales, and is delivered to the boiler house by means of dump-bottom battleship-type regular railroad cars. The coke is unloaded from the coke cars into a bifurcated hopper equipped with shuttle feeders. The coke is then conveyed to a crusher, where it is crushed or sized to one half-inch or under. From the crusher the coke is elevated by a bucket conveyor to a belt conveyor which traverses the length of the coke bunker. As the crushed coke contains as high as 14 per cent water and is sometimes oily in nature, it does not readily feed from the bunkers to the pulverizers unless the slope of bunker bottom is steep. The coke bunkers were, therefore, designed with four sides of bunker outlets sloping 60 degrees. With this design no coke remains in the bunkers longer than 48 hours when the boilers are operating at normal rating. The coke is sized to one half-inch or under by means of a ring-type crusher. The sizing of the coke is important in order to obtain a constant

feed to the pulverizers. No coke-weighing equipment is used in the boiler room, and daily boiler efficiency is calculated on amount of coke delivered to the bunkers each day. Monthly efficiencies are calculated more accurately by starting and ending the month with a full coke bunker.

The refinery gas burned is measured by means of an orifice plate and a recording differential- and static-pressure meter. Gas volumes as metered are corrected for specific gravity, temperature, and pressure. The heating value of the refinery gas is determined by a Junkers-type calorimeter. The fuel oil burned is determined by tank gages. Corrections for temperature are made on quantity of oil determined by tank gage.

Coke is pulverized by means of ball-type pulverizers. There are two No. 10 Bonnot pulverizers per boiler. The pulverizers have a rated capacity on coal of 10,000 pounds per hour, but are only required to pulverize approximately 6000 pounds coke per hour at maximum boiler capacity. The moisture content of the coke averages about eight per cent by weight, but at times contains a maximum of

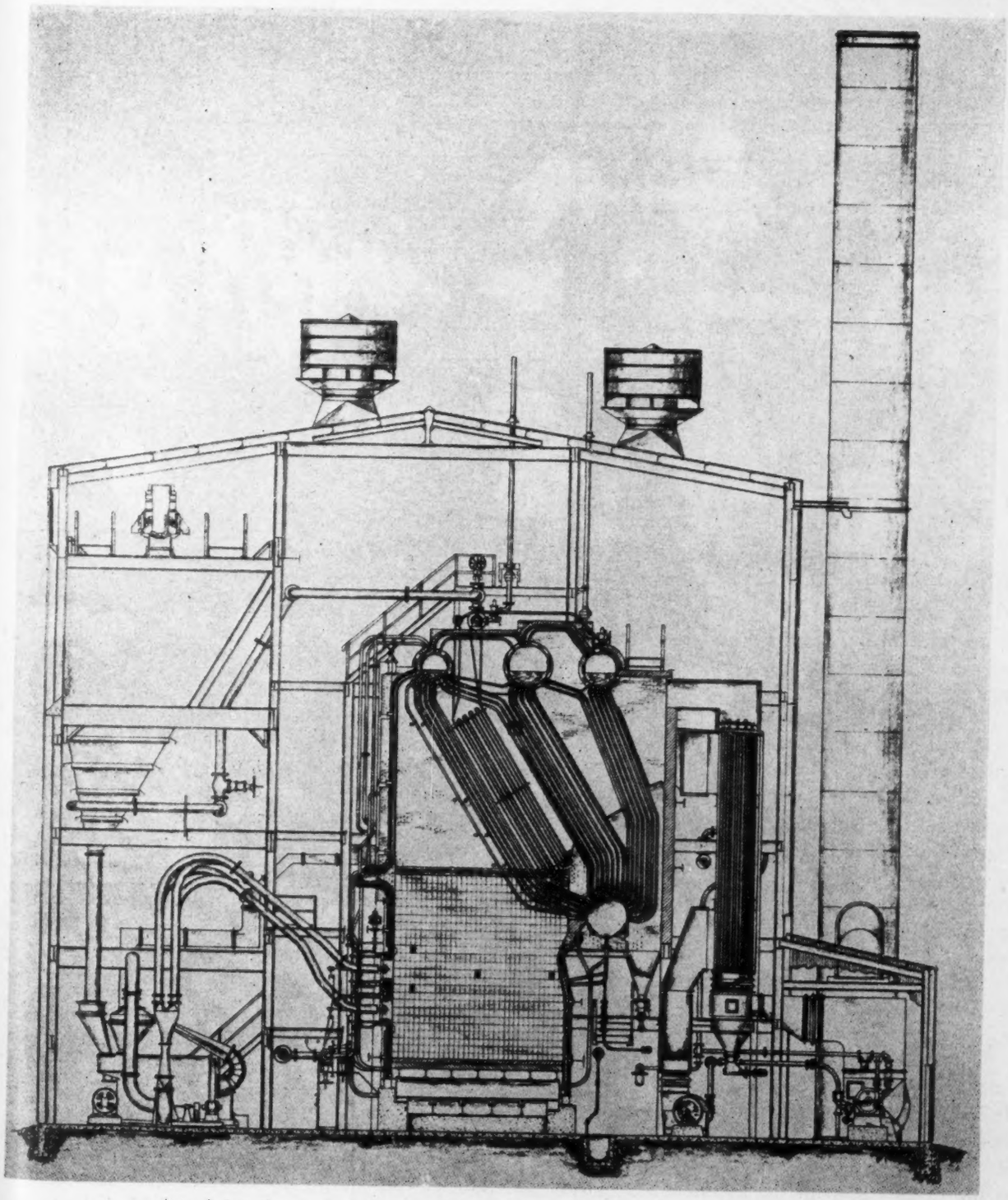


FIGURE 1

Sinclair Refining Company's Layout of Boilers, Pulverizers, Forced- and Induced-Draft Fans, Coke Bunkers, and Stack. Note That All Operating Equipment Is at Operating Floor Level.

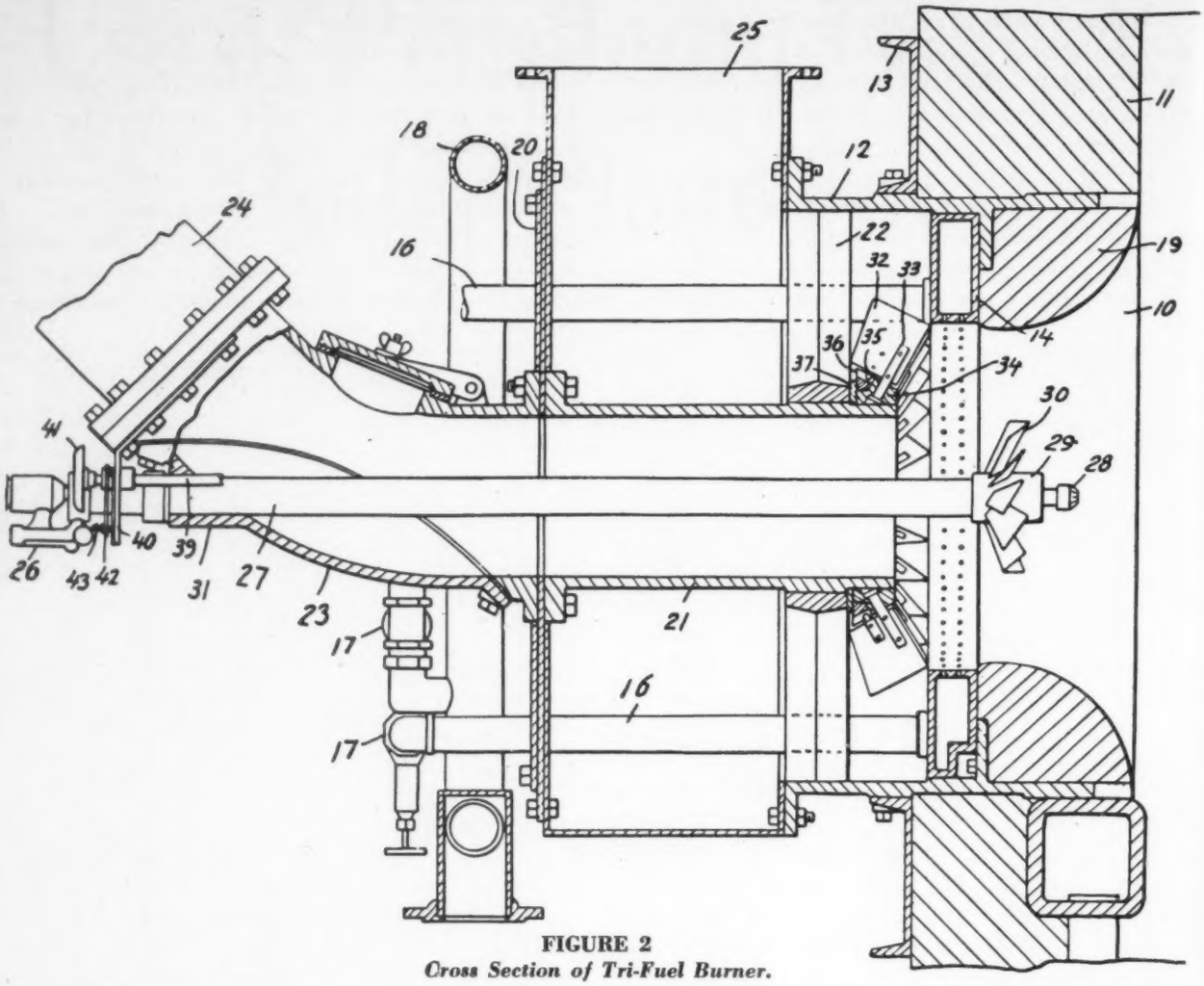


FIGURE 2
Cross Section of Tri-Fuel Burner.

about 14 per cent by weight. Fine pulverization is required on low-volatile coke, and screen tests show an average of 84 to 88 per cent passing through a 200-mesh screen with less than 0.5 of one per cent on a 50-mesh screen. Ball consumption per ton of coke is less than one fourth pound. No repairs have been made to date on mill liners or exhausters.

As the steam requirement for the refinery is substantially constant, with less than 10 per cent variation from hour to hour or from day to day, no automatic combustion-control equipment was installed. For ease of operation, push-button control is used to operate the forced and induced draft dampers and the steam supply to turbines which drive the forced and induced draft fans. Each boiler is equipped with a Bailey boiler meter showing air flow, steam flow, steam temperature, and feed-water temperature. Indicating draft gages and air and flue-gas temperature recorders are also installed on each boiler. Each boiler is also equipped with water-level indicators and recorders at operating floor level.

As the steam output of the two new boilers supplies the major portion of the refinery steam demand, it is imperative that no boiler interruptions occur. Under these conditions the forced- and induced-draft fans are steam-turbine driven, as there is always a steam supply available. An electric supply interruption would force shut-down of both boilers if fans were motor-driven. The pulverizers are motor-driven; and, when an electric failure occurs, oil and gas make up the fuel supply and the boilers continue at full capacity. The forced-draft fans are directly connected to the turbines, whereas the induced-draft fans use a reduction gear.

The burners are so designed as to burn pulverized petroleum coke, refinery gas or any grade of fuel oil. The burner design is shown in Figure 2. The fuel-oil burners are inserted through the small two-inch pipes in the center of the burners. As the fuel oil burned is approximately 0 degree gravity, A. P. I. and contains an appreciable amount of suspended solids, steam-atomizing oil burners are used. The pulverized coke and the primary air supply are delivered to the furnace through the large center pipe and are deflected by means of a distributor into the secondary air stream. The gas burner consists of six separate alloy sections forming a gas ring, which is placed just behind the burner tile that surrounds a set of adjustable secondary-air vanes.

The original installation did not have adjustable secondary-air vanes, and it was impossible to maintain ignition without the use of refinery gas or fuel oil when burning low-volatile coke. After the secondary-air vanes were installed, it was possible to burn satisfactorily petroleum coke with a volatile content of less than five per cent without the use of gas or fuel oil to maintain ignition. The position of the secondary-air vanes is changed with change in boiler rating. The lower the boiler rating, the nearer the vanes are to being closed. At full load the secondary vanes are about two thirds open, and at half load the vanes are about one quarter open. The only repairs made to date on these burners has been one replacement of the refractory tile in front of the gas-burner rings.

The boiler tubes have not slagged up in the first pass, and no difficulty has been encountered in maintaining capacity on account of slagging-up first pass. The internal surfaces of boiler tubes and water wall tubes are clean after a year's operation. No turbining of boiler tubes or water wall tubes has been necessary. After six months' continuous service there was not enough mud deposit in tubes, headers or drums to fill a two-quart pail.

The make-up boiler feed water is supplied from water wells, and repeated analyses show very uniform water characteristics. The feed water supply contains an amount of hardness which makes treatment necessary. Proper boiler operating conditions demand a water of low hardness to prevent scale. Zeolite softening equipment was selected, preceded by an ample filtration system to eliminate any possibility of getting any sand from the water wells into the treating system. The raw water is delivered to the filters and softeners direct from the water wells, and from the softeners to oil-condenser boxes on stills, and then to a storage tank. Steam turbines or electric-driven pumps deliver the water from the storage tank through a continuous blow-down low-level heat exchanger to an open-type deaerating feed water heater. Daily tests for oxygen are made. The water from the feed water heater is delivered by electric or steam-turbine driven pumps through a high level heat exchanger to the boilers.

Continuous boiler blow down equipment is employed as a means of preventing the building up of high boiler concentrations. High boiler concentrations cause priming or carry-over of dissolved or suspended solids into superheater tubes, pipe lines, and turbines. The

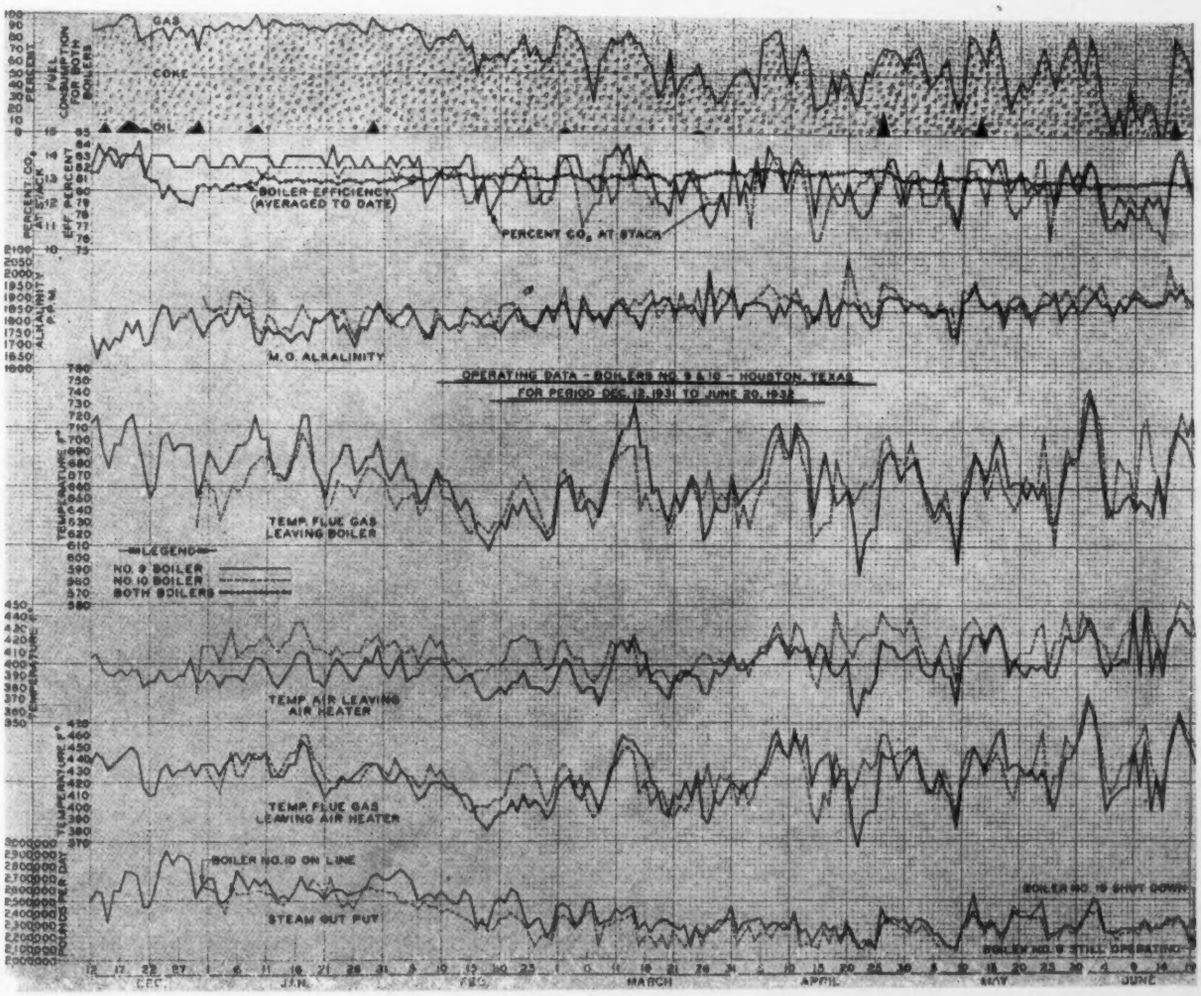


FIGURE 3

Average Daily Operation for Sinclair's Boiler Plant Addition for Period from December 12, 1931, to June 20, 1932.

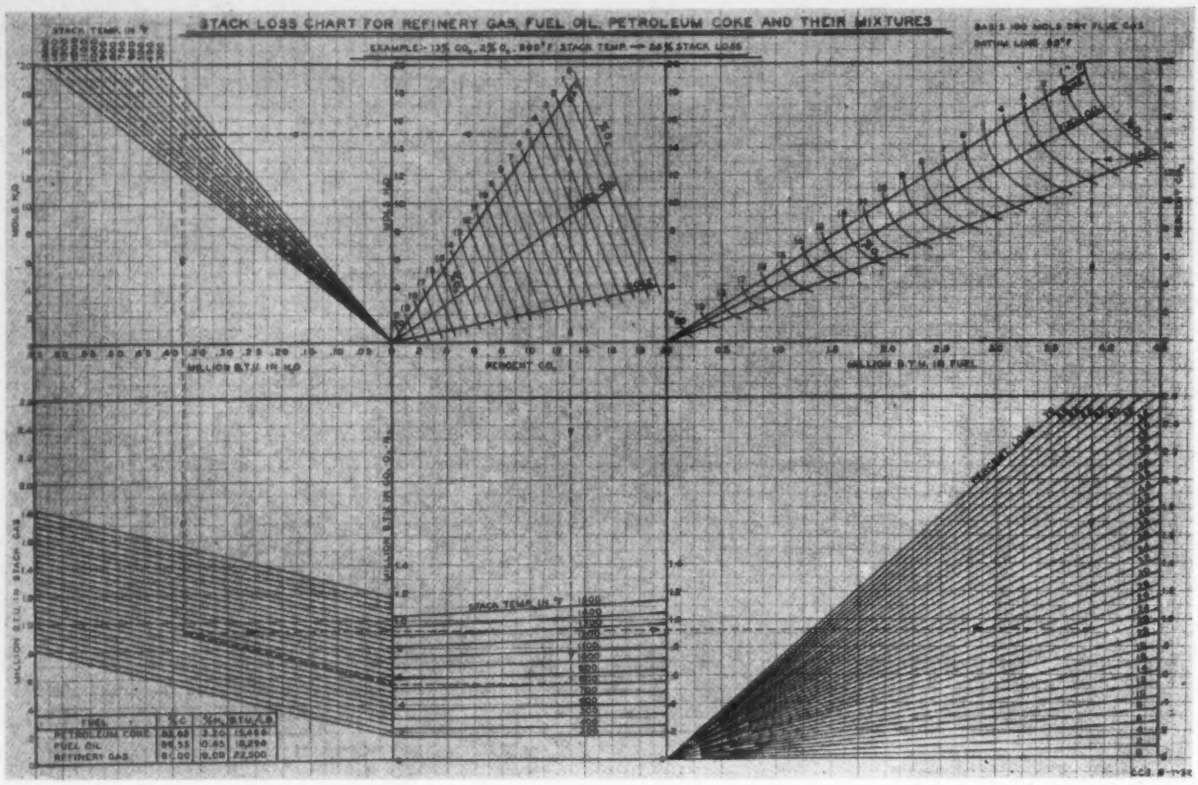


FIGURE 4

Stack-Loss Chart for Sinclair's Refinery Gas, Fuel Oil, Petroleum Coke, and Their Mixtures.

percentage of blow down is determined by daily tests for boiler concentration, and is held to a pre-determined amount. About 10 per cent of the water fed to the boilers is blown down to keep the methyl-orange alkalinity about 1800 to 2000 parts per million. Figure 3 shows the methyl-orange alkalinity of both boilers.

The blow-down water leaving the boiler contains an appreciable amount of heat, which is recovered by means of a high-level heat exchanger between the boiler-feed pump and the boiler, and a low-level exchanger between the booster pumps and the feed water heater. The blow-down is controlled by individual boiler-float control boxes.

The water fed to the boilers is measured by means of an indicating and recording Venturi meter. Any oil that may be found in the exhaust steam is eliminated by use of an oil separator.

Figure 3 shows average operating data for the six months' period December 12, 1931, to June 20, 1932. Both boilers were in continuous operation from December 30, 1931, to June 20, 1932. No. 9 boiler operated continuously from December 12, 1931, to July 5, 1932. The carbon dioxide data as shown in Figure 3 consists of grab samples once a shift, and are not a continuous record but are fairly representative. The wide variations in gas and air temperatures are caused by variations in boiler cleanliness brought about by variations in amount of caustic coke burned. It is noted that during the months of December, 1931, and of January and February, 1932, the major portion of the fuel consumed was petroleum coke; whereas, for the months of March to June, 1932, inclusive, the quantity of petroleum coke consumed was approximately 50 per cent of the total fuel consumption. The cause of the decreased coke consumption was on account of surplus refinery gas which could not be consumed on the other fuel-burning units throughout the refinery. Due to the nature of refinery operations there is an increased production of refinery gas during the summer months; and, as there is no adequate means of storing the gas, it is necessary that it be consumed in the boiler plant. If the gas were not burned at the boiler plant, it would have to be wasted; therefore, in order not to waste the refinery gas, it is necessary to reduce the coke consumption.

The small amount of fuel oil consumed was caused by electrical power interruptions, which necessitated shutting down the coke pulverizers until the electrical difficulties were remedied. During the days of June 14 and 15 it was necessary to operate both boilers on refinery gas in order to consume the excess of refinery gas produced.

Due to the burning of either one, two, or three fuels simultaneously and not knowing the percentage of each fuel burned, it was difficult to determine the approximate efficiency at any particular time. Therefore, in order to get a check on efficiency, a stack loss chart was calculated. This chart is shown by Figure 4. The use of this chart enables the operators to tell stack

losses when the per cent of carbon dioxide, and the per cent of oxygen and the temperature of flue gases leaving the air pre-heater, are known, regardless of kind or quantity of each fuel burned. The per cent stack loss is determined from the chart by the following steps:

Step 1: Start with the upper middle chart, and determine the mols of water vapor formed per 100 mols of dry flue gas.

Step 2: The upper left chart shows the B.t.u. in the water vapor formed per 100 mols of dry flue gas at the flue gas temperature determined by test.

Step 3: The lower middle chart shows the B.t.u. in the carbon dioxide, oxygen, and nitrogen per 100 mols of dry gas at the flue gas temperature determined by test.

Step 4: The lower left chart shows the addition of the B.t.u. in water vapor formed and in the dry flue gas per 100 mols dry gas at the flue gas temperature determined by test.

Step 5: The upper right chart shows the B.t.u. in the fuel per 100 mols of dry gas.

Step 6: The lower right chart shows the total B.t.u. loss in stack gas and the per cent stack loss. The use of this chart enables the operators to check the stack losses readily and easily and to determine the approximate boiler efficiency. The accuracy of this chart depends entirely on the accuracy of the flue-gas analysis and the correctness of the stack temperature.

The combustion chart was compiled from average fuel analyses of Sinclair fuel oil, refinery gas, and petroleum coke. If fuels of different analyses are used, another chart would have to be made. However, there would have to be a marked change in heating value of fuel or fuel analyses before another chart would be required. If the heating value of the fuel changes, the per cent carbon and per cent hydrogen will change, and the per cent stack loss by the combustion chart will be approximately correct. For all practical purposes the combustion chart may be used to determine per cent stack loss when burning any petroleum product.

When burning fuels of low volatile content, there is usually a high fixed-carbon loss due to unburned carbon passing up the stack. In case of petroleum coke, the fly ash consists primarily of unburned carbon. Laboratory tests of fly ash show a carbon content of approximately 97 per cent. An innovation of this boiler plant is that the fly ash deposited in third pass of boiler, in bottom of air heater, and in base of stack is returned to the furnace for re-burning. This fly ash is returned to the furnace in between the water-wall tubes and about one foot above the slag level. Experimental work was conducted by returning the fly ash to the furnace by means of compressed air jet. The final arrangement consists of an exhauster taking suction on bottom of third pass, under air pre-heater and base of stack. Some flue gases were, therefore, returned to the furnace; and, in order to lower temperature of recycled flue gas, cold air was allowed to be drawn into suction side of exhauster piping. The return of the fly ash to the furnace practically eliminated any fly ash being delivered to the atmosphere. Some of the coke burned has no caustic content; and, when this coke is burned, the appearance of the flue gas from the stack approaches that of fuel oil firing.

Sinclair Refining Company maintains its own engineering department for the complete design and construction of its various units, both in power and refinery fields. Much consideration was given to the boiler plant design for ease of operation, reduction in operating labor and repairs, accessibility, reliability, and practically continuous operation. The design has made possible the long runs as shown in Figure 3. Sinclair Refining Company has pulverized-petroleum coke-burning installations on boilers at the East Chicago, Indiana, Marcus Hook, Pennsylvania, and Coffeyville, Kansas, refineries. Sinclair Refining Company also has two oil-still furnaces at the Houston refinery and one at the East Chicago refinery which operate satisfactorily on pulverized petroleum coke.

The Nitrobenzene Process for Lubricating Oils

(*Continued from page* 567)

placed in iron bombs and heated for definite periods in an oil bath, after which the nitrobenzene was determined by titration with titanous sulfate. Again (Figure 9 C) 342°F. brought about no destruction of nitrobenzene, although 401°F. did.

Considering Figure 9 as a whole, each method arrived at the same finding — that little or no nitro-

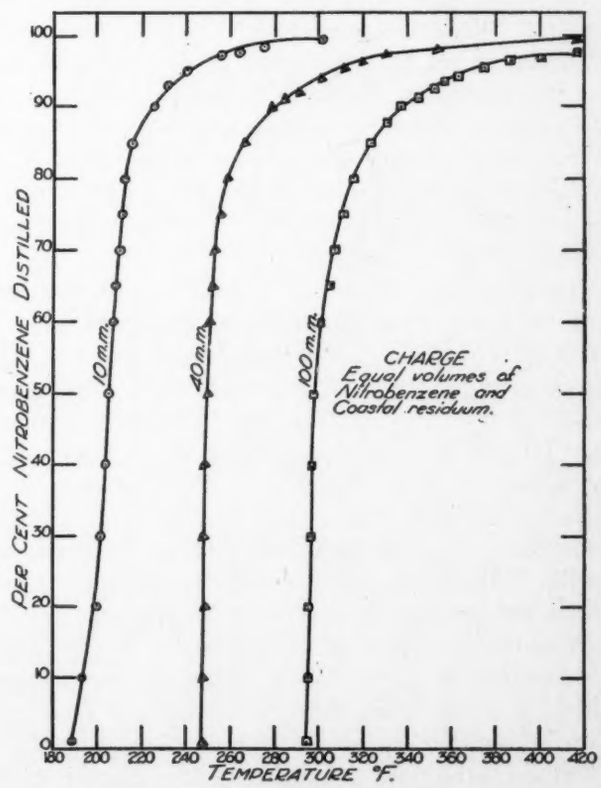


FIGURE 10
Recovery of Nitrobenzene from Oil Mixtures.

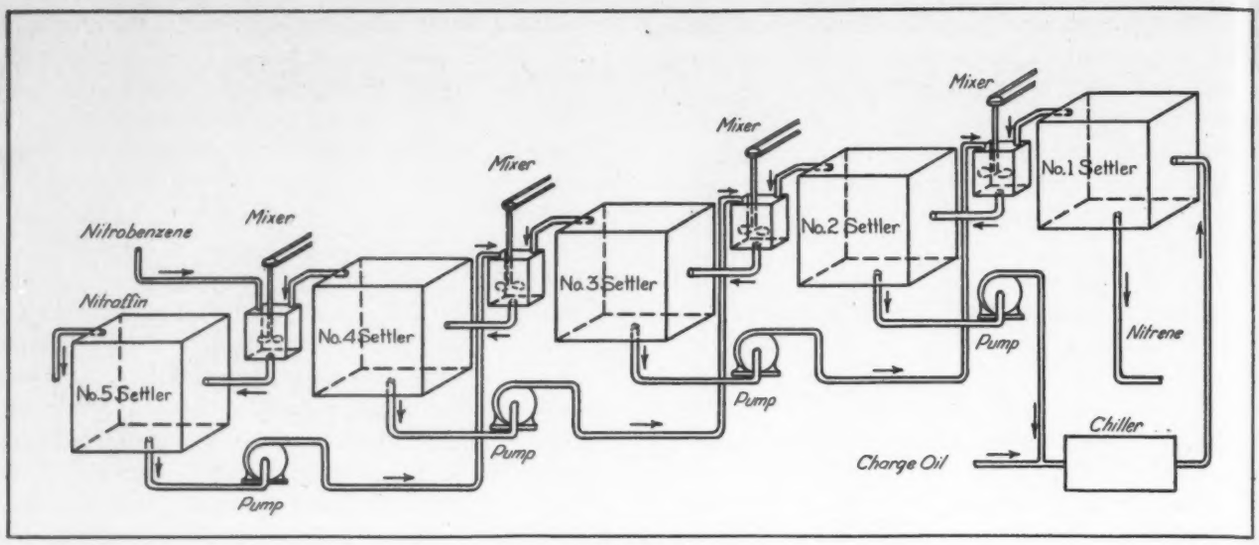


FIGURE 11
Diagram of Counter-current Extractor

benzene is destroyed below about 350°F. Figure 10 demonstrates how readily the solvent may be removed without reaching this temperature.

The sources of nitrobenzene loss and their extent, based on the volume of nitrobenzene charged, are:

1. Plain leakage and evaporation from pumps, gaskets, etc. This can and must be cut to negligible quantities.
2. Decomposition in evaporator ..... 0.06 per cent
3. Nitrobenzene content of stripped products 0.01 per cent
4. Solution in condensate from strippers.... 0.004 per cent
5. Vacuum pump exhaust after scrubbing.. 0.01 per cent

Total loss ..... 0.084 per cent

For cost calculations a loss of 0.2 per cent (safety factor 2.4) was employed.

DESCRIPTION OF THE PLANT

The plant required for the process consists of two parts: 1, the continuous five-stage counter-current extractor, in which the charge oil is separated into the "nitraffin" and "nitrene" fractions; and, 2, the nitrobenzene recovery system, which consists of an evaporator-condenser and a steam stripper for each of the two products from 1, together with a nitrobenzene absorption tower for scrubbing the gases passing to the vacuum pump.

The extractor consists of five rectangular settlers, each of which provides approximately one hour of settling. The general arrangement of the stages is shown conventionally in Figure 11. The inter-stage mixers are so placed that the "nitraffin" (usually waxy) layer from one stage flows over a weir into the mixer, is there mixed with the "nitrene" from the second succeeding stage, the mixture passing from the bottom of the mixer into the intermediate settler. This process is repeated throughout the system as the diagram illustrates. The interface level in each settler is automatically controlled by the gravity differential of the layers. The "nitrene" layer, which is at all times fluid, is transferred from one stage to another by low-head centrifugal pumps.

The essential flow chart of the entire plant is given in Figure 12. The "nitrene" removed from the first stage of the extractor **A** is heated to 220°F. by exchangers, and then passes to the "nitrene" evaporator-condenser **B**, in which all but 1 per cent of the solvent is removed as the solution passes down through the six sections wherein the temperature of the oil is gradually raised to a maximum of 300°F. The complete removal of the nitrobenzene is accomplished in steam stripper **C** at a maximum temperature of 350°F. The absolute pressure maintained in the former unit ranges from 10 mm. to 30 mm., and is 50 mm. in the latter.

The "nitraffin" discharged from the fifth stage of the extractor is similarly handled in the "nitraffin" evaporator-condenser **D**, and the stripper **E**. The product is then ready for the subsequent treatment required for producing the finished oil. The exit gases from both **B** and **D** are scrubbed by the incoming oil in **F** before passing to the vacuum pump.

COST OF OPERATION

An exact statement of costs and economies cannot be given, as no adequate operating data are yet available, and unit costs will vary in different refineries. The following calculations are based upon careful design and experimental data, and present a fair picture of the process. All unit costs are approximate, and should be modified to suit individual refinery experience. The unit service requirements and their approximate cost are given in Table 9.

TABLE 9
Service Requirements for Nitrobenzene Extraction

	Net Consumption† Per Gallon		
	Oil	Nitrobenzene	Assumed Unit Cost
Steam* (150 lb. per sq. in., gage), lb.	2.8	2.5	$0.35 per thousand lb.
Water (85 deg. F.), gal.	8.5	10.5	6.00 per million gal.
Power, kwh.	0.007	0.007	0.01 kwh.
Refrigeration,* tons	0.00063	0.00072	0.40 per ton
Nitrobenzene, gal.		0.002	0.80 per gal.

*25 deg. recovery assumed.
†Items for oil and nitrobenzene should be added.

Let us assume that we are producing a heavy motor oil from a mixed-base crude such as is out-

lined in Table 7, and that the daily throughput is 1,000 (50-gallon) barrel oil charge. The processing costs are summarized in Table 10. Fixed charges for labor, repairs, and general expense are assumed to be $100 per day; while those for overhead, depreciation, and royalty are excluded.

The processing cost, on the basis of these assumptions, is of the order of $0.37 per barrel of oil charged; or, assuming that the total processing cost must be borne by the "nitraffin," and that the "nitrene" is given charge stock value, the cost of the nitrobenzene process is $0.71 per barrel of "nitraffin" produced.

TABLE 10
Cost of Operation

Item	Service Requirements: 1,000 Bbl. Oil	1,400 Bbl. Nitrobenzene	Cost
Fixed charges	.....	.....	$100.00
Steam, thousand lb.....	140	175	110.00
Water, million gal.....	0.42	0.74	6.95
Power, kwh.	350	490	8.40
Refrigeration, tons	31.5	50.4	32.80
Nitrobenzene loss, gal...		140	112.00
Total operating cost.....			$370.15

CONCLUSION

It has been the endeavor of the authors to present in this paper the salient features of the nitrobenzene extraction process, and to avoid the inclusion of detail; which, though of much value and interest, would confuse the over-all picture. Sufficient data have been included so that general comparisons may be made with the various refining processes now available for the production of lubricating oils.

The essential characteristics of a good motor oil are taken to be a flat viscosity-temperature slope and a low carbon residue. In general, overhead products enjoy an advantage, with respect to carbon residue, over residual products. Pennsylvania oils exhibit excellent viscosity-temperature slopes, but poor carbon residues; while the reverse is true for Coastal oils.

It has been demonstrated that:

1. A motor oil, superior in every respect, can be produced by nitrobenzene extraction at a reasonable cost.
2. This process insures flexibility with regard to crude source and viscosity of charge.
3. Exceptional oils for special purposes may be produced without modification of the plant.

BIBLIOGRAPHY

[1] Bahlke, Barnard, Eisinger, and FitzSimons, J. Soc. Automotive Eng., **29**, 215 (1931).
[2] Hill and Coats, Ind. Eng. Chem., **20**, 641 (1928).
[3] Dean and Davis, Chem. Met. Eng., **36**, 618 (1929).
[4] Houghton and Robb, Ind. Eng. Chem., Anal. Edn., **3**, 144 (1931).
[5] J. Soc. Automotive Eng., **29**, 247 (1931).
[6] Ferris, Birkhimer, and Henderson, Ind. Eng. Chem., **23**, 753 (1931).
[7] Weir, Houghton, and Majewski, Ind. Eng. Chem., **22**, 1293 (1930). (Fig. 2).

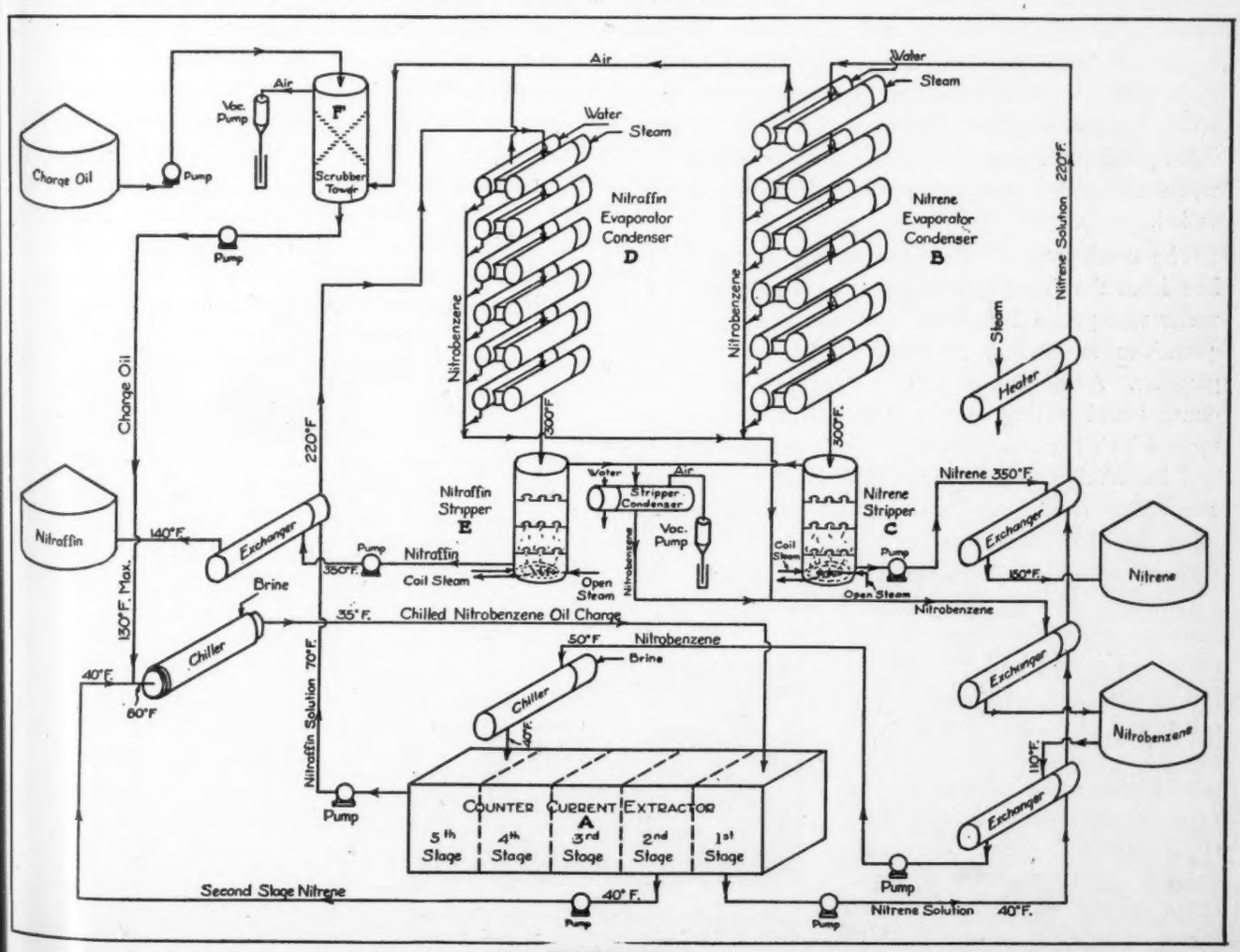
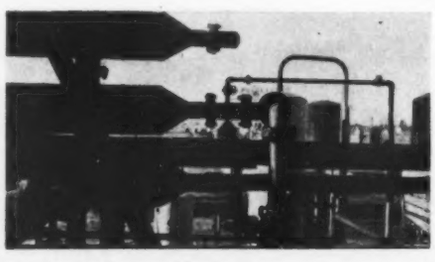


FIGURE 12
Flow Chart of Nitrobenzene

Water Injected Into Gasoline Stream Cuts Refining Losses

BECAUSE unusual hot weather prevailed in Wichita Falls, Texas, during summer months, gasoline stream from the submerged condensers and enclosed after coolers in the Taxman Refining Company plant ran as high as 104°F. Strict attention of the operators to the loss in circulating water by maintaining the proper packing in centrifugal pumps, preventing loss of efficiency by preventing foreign matter from entering the pumps did not remedy the situation. Louvre tower decks were scrubbed to provide a maximum distribution of water when pumped over them. Each detail was looked into to provide condenser water with a temperature as low as atmospheric conditions would permit. Yet the stream temperature of the gasoline entering the accumulator or run tank was so high that an appreciable refining loss at this point was constantly confronting the operators. Pump capacities were large enough that a sufficient amount of water could be circulated, but the principal difficulty was found to be an inadequate amount of condensing and cooling surfaces when extremely high atmospheric temperatures prevailed.

The condensers on the straight run gasoline vapor line from the fractionating tower were submerged and water was pumped into the condenser box in sufficient quantities to prevent steaming while condensing the gasoline. After-coolers were placed beside the condensers and resting on the roof of the control room upon which the condenser box was placed in the original installation. These after coolers were constructed at the plant from joints of 12-inch pipe, having one-inch tubes placed inside and welded to tube sheets at each end through which the condensed gasoline was carried. Circulation through these sections was provided for countercurrent flow between gasoline and water, and through the fall, winter and early spring periods of the year, the cooling of the stream was sufficient to prevent appreciable losses due to the escape of uncondensed light fractions distilled from the crude charge. When summer temperatures prevailed, however, the stream temperature was too high for economical operation.



Showing the method of connecting one-inch water line to line carrying condensate to after coolers in Taxman Refining Company, Wichita Falls, Texas.

Preparations were in progress for the installation of additional after cooling equipment which would have added to the investment of the plant when Jimmie Hinds, plant superintendent, decided that the same results might be obtained without adding any equipment to that already installed by pumping a stream of water directly into the gasoline as it entered the aftercoolers from the submerged condenser sections.

The water line from the circulating pumps serving the aftercoolers branched from the main line leading to the condenser box. A back pressure was held on the discharge of the water pumps by gate valves at the entrance of the condenser box and on the line before it entered the shell of the after-coolers, making it possible for this operation to be carried out without the danger of gasoline and vapors backing up into the water system.

A one-inch line was tapped into the two-inch leading from the main to the after coolers, leading it to the forward end of the first after-cooler section, connecting it by using a short nipple in the gasoline inlet, using flanges on each end. A check valve was placed in the one-inch line between the point of connection with the two-inch and the control gate which permits the operator to admit a sufficient volume of water to the head of the after cooler sections. The water coming in direct contact with the gasoline liquid and uncondensed vapors has reduced the temperature at the accumulator, or run tank, an average of 15°F. During the latter part of July, 1932, when the atmospheric temperature soared and remained around 103 to 106°F. the stream entering the accumulator tank was maintained consistently around 90°.

No harmful conditions have presented themselves through this operation, but rather an apparent beneficial one other than the reduction of stream temperature. The gasoline is washed and treating costs have been lowered slightly. Water and gasoline are received in the common accumulator and separated by removing the water from the base through a water trap.

The Winkler-Koch *Cracking Unit*

M. KALITA

Gronznenskii Neftyanik: 1931, No. 8-10, 82-6
Translated from Russian by A. A. Boehtlingk

THE accompanying discussion relates of a series of experiments with the Winkler-Koch cracking units as operating in Russia. M. Kalita reviews the work done in regard to recycling and determination of the time of recycling in all sections of the twin-furnace installation.

During the past year or two a number of highly interesting articles have been published in the Russian technical literature having to do with operating technique in the cracking field, for the most part being based on Winkler-Koch, Vickers and Jenkins units, and on two processes developed in Russia. Translations at hand indicate that much of interest is included in the form of progress reports. They are available from the translator of this present work.

IN Grozny the operating cracking processes are Winkler-Koch, Jenkins and Vickers. The cracking in the Winkler-Koch unit is effected at high pressure, similar to the Vickers units, being operated at a pressure of 40 atmospheres.

The lay-out of the Winkler-Koch process under discussion is shown in Figure 1. The fuel oil is pumped at seven atmospheres pressure in succession through two distillate-vapor heat exchangers into the low pressure furnace and thence into the evaporator after having been united with the stream of the product coming from the high pressure coil. A separation of heavy cracked residue from the lighter parts is effected in the evaporator, the former is discharged through the bottom of the evaporator and then cooled in a cooler. Vapors are passed from the evaporator through one heat exchanger and admitted into the bubble tower. They are then passed through the second heat exchanger from the middle of the bubble tower and readmitted into the lower part of the upper section of the bubble tower. Pressure distillate is taken off from the top of the bubble tower, passed into the gas separator after undergoing condensation and cooling. Condensate formed in the bottom of the tower is passed by the hot pump at a pressure of 40 atmospheres into the high pressure furnace where it is cracked. Thus in the Winkler-Koch cracking unit a gas oil removed from the fuel oil proper in the low pressure coil and a cycle stock obtained by repeated cracking of the gas oil is cracked rather than the total fuel oil. Should the amount of the condensate obtained in the bubble tower be insufficient to feed the high pressure coil (this happens when the fuel oil is too heavy), then gas oil may be admitted into the tower.

The first twin Winkler-Koch unit (the single unit) was put in operation in the later part of July, 1930. At present two more units are in operation. The first single Winkler-Koch unit started to operate July 27, 1930, and it has now 10 cycles to its credit. Three of these cycles were only of a short duration, e.g. the first cycle lasted only 9.5 working days and 8.25 idle days, the sixth had 21 and 7 days and the eighth 5.5 and 4.5 days respectively. Forced shutdowns occurred in the sixth and eighth cycles because of excessive coke formation in the soaking tubes of the high pressure furnace. The other cycles proved that the unit can be operated for 30-40 days without interruption. In this unit a one to two mm. layer of coke is deposited only in the tubes of the high pressure furnace and a coke deposit three to four mm. thick is observed in the return bends of the tubes, provided the operating conditions are normal. The removal of the coke from the tubes took originally much time due to lack of experience. The time required for this operation was however considerably shortened after the necessary experience was gained, it then required only three to five days. The efficiency of the apparatus amounted to 80-90 per cent.

The second part of the unit which was placed in operation in the later part of November made 14 cycles, which, however, were only of a short duration, because the incorrect registration of the measuring equipment caused the coking up of the pressure reduction valve.

This part of the unit worked under normal conditions beginning with the end of January, the cycles being of longer duration and the efficiency of the apparatus increased to 85 per cent. Changes in the construction of this unit were made after the second shut-down. They consisted of the elimination of two partitions in each of the heat exchangers which caused a better performance of these exchangers. A comparison between the first and the second cycles of the unit is shown in Table 1.

Table 1

	Temperature °C	
	First Cycle	Second Cycle
High Pressure Furnace Temp. of Fire Gases		
Above the bridge wall	620	635
Below the convection tubes	415	435
In the smoke stack	249	248
Low Pressure Furnace Temp. of Fire Gases		
Above the convection tubes	532	482
In the smoke stack	217	302
Temperature of Products *Heat Exchanger*		
Fuel oil outlet from first heat exchanger	.....	198
Fuel oil outlet from second heat exchanger	312	322
Vapor inlet into first heat exchanger	259	250
Vapor outlet from first heat exchanger	.....	226
Vapor outlet from second heat exchanger	321	354
Fuel oil at the outlet from the low pressure coil	375	383
Inlet into the high pressure coil	310	321
Outlet from the first section of high pressure coil	344	357
Outlet from the second section of high pressure coil	.....	400
Outlet from the radiant tubes of the high pressure coil	478	479
Outlet from the soaking end of the high pressure coil	485	490
Lower end of evaporator	400	404
Upper end of evaporator	407	405
Upper end of the bubble tower	193	193
Pressure Pounds per Square Inch		
Inlet of low pressure coil	102	110
Outlet of low pressure coil	86	93
Inlet of high pressure coil	600	600
Outlet of high pressure coil	400	400
In the evaporator	33	33
In the bubble tower	26	26
In the gas separator	19	

This table shows that vapors passing from the evaporator through the second (passed by the fuel oil) heat exchanger had a smaller decrease in temperature (405°—354°= 51°C. instead of 407°— 321°= 86°C.) but the fuel oil was preheated to a higher temperature (322° instead of 314°C.) and therefore less heat was required in the low pressure coil to heat the fuel oil to a higher temperature (383° instead of 375°C.).

Fuel consumed by this unit (third cycle) is not checked accurately. When the unit is started, because of the absence of gas, liquid fuel is used which can be recorded without difficulties. However, when the unit is in operation gas produced by the unit is burned and the gas can not be recorded because of the absence of a meter. When the unit is started about nine per cent of liquid fuel is consumed.

In a special run undertaken in April, 1931, for the purpose of determining the fuel consumption, fuel oil only was used instead of gas. This resulted in the consumption of 8.9 per cent fuel oil calculated on the gas oil used as feed stock (at this time gas oil was used as cracking stock in this Winkler-Koch unit). The water consumption is checked by meters. It varies greatly amounting to 1500 to 4000 metric tons in 24 hours. Steam and electricity, however, could not be measured because of the absence of meters. At present the approximate amount of these two items has been roughly calculated and it amounts to about 150 kilograms of steam and 0.39 kilowatt of electric energy per ton of cracking stock treated.

Table 2

The average daily throughput of the unit in the third cycle.

PRODUCT	In Metric Tons	Percent
Fuel oil used (stock)	518	100.00
Gas oil used (stock)	17	
Pressure distillate obtained	180	33.6
Cracked residue obtained	295	55.2
Losses, gas and coke	60	11.2
Gas only (approximate)	.....	8.0

When cracking gas oil (April 1931) the daily throughput amounted to:

	Metric Tons	Per Cent
Gas oil cracked	440	
Pressure distillate obtained	200	45.45
Cracked residue obtained	140	31.81
Cracked gas oil obtained	58.4	13.27
Cracked gases, coke and loss	41.6	9.47

The properties of products obtained in the Winkler-Koch unit during the third cycle are given in Table 3.

Since the Winkler-Koch unit works with a complete recycling of the charging stock the question appeared justified, how does the cracked condensate obtained as a result of numerous recycle operations behave in cracking? Is there any slowing down of the cracking process in connection with the cracked condensate's steady increase in gravity towards the end of the cycle? The Groznuii Petroleum Research Institute, therefore, carried out continuous observations of the cracked condensate during the entire cycle of the unit. It was found that the gravity of the cracked condensate does not increase toward the end of the cycle even in its heaviest

Table 3

PRODUCT	Specific Gravity	Flash Point	Engler Viscosity	Pour Point	Percent Coke	Engler Distillation °C											
						I.B.P.	100	160	175	200	225	250	275	300	%	Res.	Loss
Stock fuel oil.....	0.898	85°C	1.7 at 100°C	34°C	Max. 0.5%	230	....	....	.....	....	.....	1.5	3	9	....	....	....
Press. distillate.....	0.757	.....	.....	.....	0.5%	38	21	52.6	61	74	91.5	....	....	.....	96	0.6	3.4
Cracked residue.....	0.954	66°	37.2 at 100°C	19°	0.5%	221	....	....	.....	....	.....	0.7	1.5	5	....	....	....
Condensate in bubble tower recycled stock...	0.897	61°	1.4 at 50°C	22.3°	0.5%	210	....	....	.....	....	.....	2.5	10	3.5	....	....	....

fractions. Experiments with cracking the condensate were undertaken at the beginning, in the middle and at the end of the cycle of the unit. Experiments showed that the velocity of gasoline formation does not decrease towards the end of the cycle and that there is no increase in the velocity of carboids (coke) formed. It is possible that the condensate is subjected to some change only at the beginning of the cycle, during a few recyclings and then its composition becomes stabilized toward the end of the cycle.

To determine this a few calculations were made which soon showed how fast the composition of the condensate is stabilized. The number of daily cycles in the apparatus was calculated as well as the duration of the condensate within the apparatus. The calculation was based on the data of the performance and the amount of stock cracked during October, 1930, (the third cycle of plant No. 1). The amount of cracked condensate passed through the high pressure coil was calculated on the basis of the oil passed by the high pressure pump which, at 11 strokes per minute, passes 710 metric tons of stock through the coil in 24 hours. The amount of products obtained in the unit when recalculated on the cracked condensate passed through the high pressure coil is then expressed by the following figures: Pressure distillate 25.3 per cent, gas six per cent. The amount of condensate which is present in the coil in a given time can not be calculated by the average temperature of the furnace, because cracking takes place in the roof tubes and the soaking section of the coil which is accompanied by a strong generation of vapors. Therefore, the amount of condensate in the roof tubes and the soaker was calculated separately. In the first and second preheater sections of the furnace, the condensate is heated from 322° to 400°C. at 40 atmospheres pressure. Under these conditions it can be roughly assumed that the entire condensate exists in the liquid state and the weight of the product is therefore calculated on the basis of the average temperature of this section, i.e., 360°C. The amount of condensate present in the section is 2.227 metric tons basing on its capacity amounting to 3.33 cubic meters and the specific gravity of the condensate of 0.668 at 360°C. (using Cragol's equation).

By the use of Obryadchikov's equation on the state of the product in the tubes (The Heat Problems in Cracking), the volume of the product at the outlet of the high pressure furnace can be calculated. The composition of the product leaving the high pressure coil had been established by the Petroleum Research Institute of Grozneft who repeatedly recycled the cracked condensate, obtained in the bubble tower. In a unit producing 25.3 per cent pressure distillate, 70 per cent of a fraction boiling below 200°C. is obtained (see determinations) or 19.5 per cent calculated on the cracked condensate in addition to six per cent gas.

According to the Petroleum Research Institute of Grozneft 35.8 per cent of fractions boiling at 200°-300°C. and 30.7 per cent of a residue, correspond to the above amount of fractions boiling below 200°C. Assuming that at 490°C. (temperature at the outlet of the coil) and at 400 pounds (26.6 atmospheres) pressure all fractions boiling below 300°C. will be converted into the vapor state, the volume of the product discharged from the high pressure coil (according to S. N. Obryadchikov) is calculated, whereby a correction is made for the deviation from gas laws and for the solubility of the gases in the liquid. The amount of the product by weight in this part of the coil (calculated on the basis of the average specific gravity of the product, 0.483) amounts to 3.02 metric tons. The total amount of the cracked condensate present simultaneously in the high pressure coil is $2.227 + 3.02 = 5.247$ metric tons. The number of cycles in the high pressure coil is $710:5.3 = 134$ and the period the product is kept in the coil amounts to about 10 minutes. The number of cycles of the radiant and soaking tubes is 235 while the coil stays in these tubes during six minutes.

NUMBER OF CYCLES OF THE CONDENSATE IN THE BUBBLE TOWER

The amount of condensate present simultaneously in the bubble tower is 12.5 metric tons when the level of the condensate in the tower is three meters and its temperature is 322°C. The number of cycles per 24 hours of the condensate through the bubble tower is $710:12.5 = 57$. The condensate stays in the bubble tower for about 25 minutes.

NUMBER OF CYCLES OF THE FEED STOCK THROUGH THE SYSTEM

The time required for the cracked condensate to return to be recycled was calculated for the amount of condensate present simultaneously in the tower, i.e., 12.5 metric tons. The cracking stock which amounts to

5.3 metric tons passes through the high pressure coil in 10 minutes, while 25 minutes will be required to pass 12.5 metric tons. The condensate is kept in the tower for 25 minutes. In the evaporator, vapors remain only a very short period (not more than five minutes) because the volume taken up by the vapor phase in the evaporator amounts to approximately 100 cubic meters. It is very small as compared with the volume of vapors which are passed through the evaporator from the low and the high pressure coils. Consequently the time required for the return of the cracked condensate for the recycling will amount to about one hour (assuming that five minutes are needed for its passage through the pipe lines). The number of daily cycles of the cracked condensate is 24. Thus, as may be seen, the first two days after placing the unit under stream are entirely sufficient for its stabilization.

NUMBER OF CYCLES THROUGH THE LOW PRESSURE COILS

The amount of product held by the low pressure coil is calculated on the basis of the average temperature in that coil (360°C.) at which the specific gravity of the fuel oil is 0.660 (by the Cragol formula). It amounts to 3.36 metric tons. The number of cycles per 24 hours is 518:3.36 = 154. The product is kept in the tubes for about nine minutes. The time required for passing the charging stock through the system beginning with the fuel oil and ending with the cracked condensate, used for recycling, can not be calculated at present because the amount of fraction taken off the fuel oil in one distillation in the evaporator, where a noticeable influence is also exercised by vapors of the light fractions obtained as a result of cracking in the high pressure coil, is not known.

DURATION OF RETENTION OF CRACKED RESIDUES IN THE EVAPORATOR

The level of the cracked residue is kept in the evaporator at about 4.7 meters from the bottom. It has a specific gravity of about 0.709 at 405°C. The cross section of the evaporator is about 5.9 square meters and the amount of the cracked residue in the evaporator is therefore equal to 19.8 metric tons. The number of cycles in the evaporator is 14 and the residue is retained in the evaporator for about one hour and 40 minutes. A prolonged retention of the residue at a temperature higher than used in this case may cause an excessive formation of coke and may coke up the evaporator.

It must be mentioned that the problem of dewaxing Groznuii mixed base fuel oil is not solved satisfactorily. The cracked residue obtained has a high pour point (20 to 25°C.). Experiments carried out with a mixture of the cracked residue and the pressure distillate boiling above 225°C. in the Petroleum Research Institute of Grozneft were unsatisfactory. Thus on mixing cracked residue with the pressure distillate boiling above 225°C. in a proportion in which they are obtained in the unit (100:2.5) the pour point was lowered by 2°C. and only a mixture of 100:15 had a 9°C. lower pour point than the cracked residue alone.

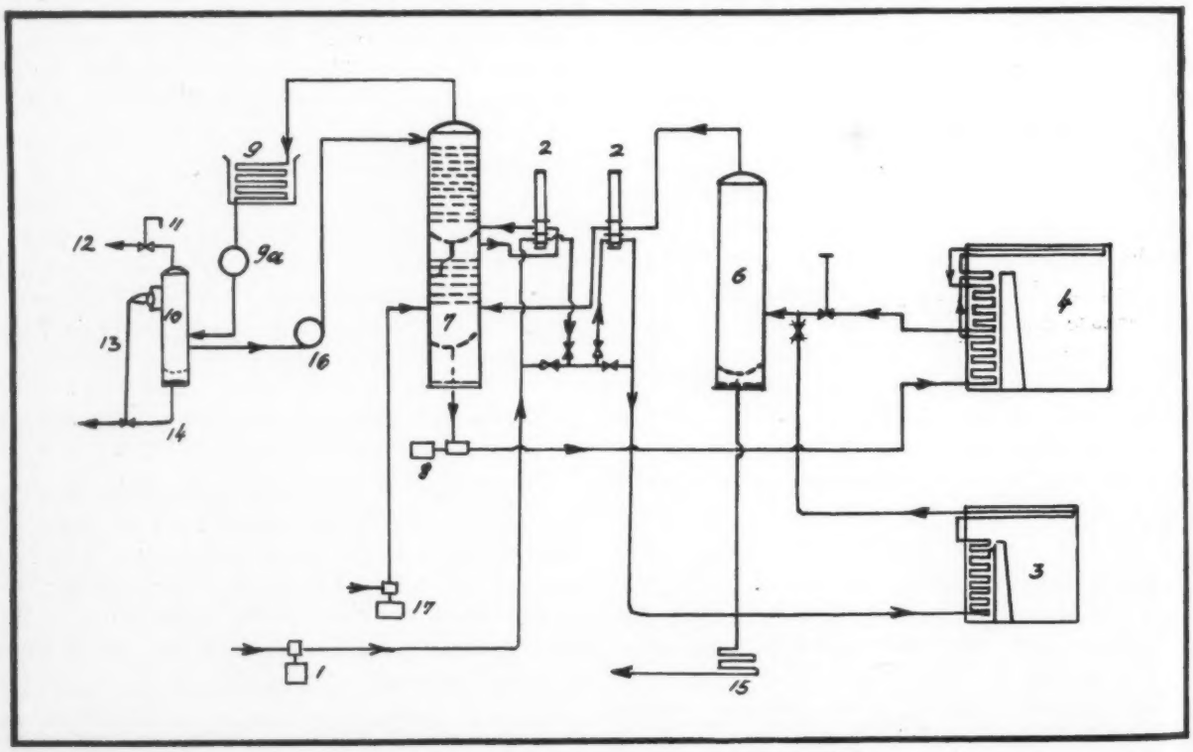


FIGURE 1—LAYOUT OF THE WINKLER-KOCH UNIT.

(1) Fuel oil pump. (2) Heat exchangers. (3) Low pressure coil. (4) High pressure coil. (5) Reduction valve which governs the pressure in the high pressure coil. (6) Evaporator. (7) Bubble tower. (8) Hot pump which feeds the high pressure coil. (9) and (9a) Condenser and cooler for the pressure distillate. (10) Gas separator. (11) Pressure release valve. (12) Gas discharge line. (13) Level adjusting device. 14) Gasoline discharge line. (15) Cooler for the cracked distillate. (16) Reflux pump for the bubble tower. (17) Pump passing the gas oil into the bubble tower.